THE ALUMINUM INDUSTRY

ALUMINUM AND ITS PRODUCTION

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THE ALUMINUM INDUSTRY
IN TWO VOLUMES

ALUMINUM AND ITS PRODUCTION

BY

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WITH THE COLLABORATION OF A GROUP OF EXPERTS FROM
THE STAFF OF ALUMINUM COMPANY OF AMERICA

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PREFACE

Widespread interest in the production, fabrication and use of aluminum has been apparent for some time. This interest has been impressed upon the authors by the great variety of questions which they are continually being called upon to answer. The available books are either out of date or do not contain authentic information on many of the subjects in which the greatest interest is being shown. It is to meet this need that the present volumes were prepared. In writing these two volumes, the authors have had the assistance of many of their associates in Aluminum Company of America and its subsidiaries. This Company has also generously contributed of the authors' time and made available to them information from its own files and experience. In addition to their own contributions, the authors have acted editorially in revising and unifying the contributions of their collaborators.

The first volume, which bears the sub-title, "Aluminum and Its Production," covers the history of the discovery of aluminum and the development of the industry, the ores of aluminum and their mining and refining for the production of pure alumina, and closes with a discussion of the production of metallic aluminum. The general treatment has been along broad lines, except in regard to the production of alumina from the ore. This subject has been treated in greater detail because of the widespread interest in the production of alumina, as evidenced by the hundreds of patents which have already been granted on this subject, and the new ones which are continually being offered to the Patent Offices in all countries. The large number of processes for the production of alumina which have already been described make it difficult for most inventors to know what has already been accomplished in this field; for this reason the available literature has been abstracted and classified with reasonable completeness. In the preparation of the chapters on the production of alumina, the original patents and publications have been consulted with very few exceptions, and it is hoped that in this way many of the errors in dates, numbers, etc., which

have crept into other publications have been avoided. In general, the dates given for the patents are the publication dates, that is, the date on which the patent became known to the public. It is realized that many of the patents on the production of alumina are impractical and will only be of interest to workers specializing in this field; for this reason most of the parts of minor importance or interest have been set in somewhat smaller type.

The second volume of this work bears the sub-title, "Aluminum Products and Their Fabrication." It deals with the properties of aluminum and its alloys, the fabrication of aluminum products and their uses in the industries.

The task of writing this book was undertaken at the suggestion of Mr. Edwin S. Fickes, vice-president of Aluminum Company of America, and his advice and assistance have been an important contribution to the work. Dr. Earl Blough assisted in the preliminary planning of the book, but other duties prevented his continuing the work. Acknowledgment is also made to Mr S. K. Colby and the many associates who have contributed their critical judgment and help.

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NEW KENSINGTON, PA.
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THE ALUMINUM INDUSTRY

ALUMINUM AND ITS PRODUCTION

CHAPTER I

THE STORY OF ALUMINUM

By

JUNIUS D. EDWARDS

The historian who would trace the story of aluminum has a comparatively easy task. It is not referred to in the writings of the "ancients," nor in classical records; aluminum is a product of the present age. Just about a hundred years ago, the first metallic aluminum that we know of was produced by an ingenious application of chemistry. Fifty years passed, however, before a cheap and convenient method of producing it was discovered. Many now living have quite literally grown up with the metal.

If the career of the metal has been short, its name has had quite a history. Pliny refers to "alumen," which we know as alum—a double sulphate of aluminum. Before metallic aluminum was ever prepared, its base came to be known as "alumina." Sir Humphrey Davy, in 1807, in London, attempted to reduce alumina by heating it with potash and electrolyzing the mixture. Although he did not succeed in preparing the metal, he became convinced that alumina had a metallic base and gave it the name "aluminum." Later he changed it to "aluminum" to correspond with the name of the oxide alumina. Still later, the spelling "aluminium" came into more or less general use. The chemical names of many of the elements end in "ium" and, for the sake of analogy, the spelling was generally accepted. It has been continued abroad to this day.

When the metal became commercially available in America, popular usage very quickly omitted one syllable from its name, and it became "aluminum" again. Technical usage followed, and the simpler spelling was adopted, informally or formally, by one technical society after another. In 1925, the American

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Chemical Society recognized this state of affairs and changed the spelling of the element from "aluminium" to "aluminum."

Oersted.

Alumina did not readily yield its metal, and even Sir Humphrey Davy, who had succeeded in preparing metallic sodium and potassium by electrolysis, was baffled by the problem. He contributed to its solution, however, for the alkali metals proved to be the necessary reducing agents. The Danish physicist and chemist, H. C. Oersted, announced to the Royal Danish Academy of Sciences at Copenhagen, in 1825, that he had obtained the "metal of clay." By gently heating potassium amalgam with aluminum chloride and distilling the mercury from the resultant aluminum amalgam, he obtained a small lump of metal having the color and luster of tin. Apparently space in the technical journals of that period was at a premium, for he contented himself with the following description of his experiments:[1]

As is well known, chemistry has succeeded, particularly in recent times, in producing compounds of chlorine and most of the combustible elements.

The compound of chlorine and aluminum (the metal of clay) was one of the few of these compounds which were left. In this case nothing could be expected from the ordinary methods of producing chlorine compounds; a new method had to be devised. Dry chlorine was led over a mixture containing pure alumina which was kept at red heat in a porcelain tube. Since the alumina thus had an opportunity to decompose on account of the heat, its combustible constituent combined with the chlorine and formed with it a volatile compound which was easily collected in a condenser, which naturally had to be provided with an exit tube for the unused chlorine and the carbon monoxide formed.

The compound of chlorine with the combustible element of the clay (aluminum chloride) is volatile at a temperature which is not much above that of boiling water; it is somewhat yellowish, perhaps however from admixed carbon; it is soft, but still has crystalline form; it absorbs water with avidity and dissolves therein with great ease and with evolution of heat. Rapidly heated with potassium amalgam, it is decomposed, potassium chloride and aluminum amalgam being formed. This amalgam is very quickly decomposed in contact with the atmosphere. By distillation without contact with the atmosphere, it forms a lump of metal which in color and luster somewhat resembles tin. Moreover, the author has found, both in the amalgam and the aluminum, remark-

[1] OERSTED, H. C., Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger, pp. 15, 16 (1824–1825).

able properties which do not permit him to regard the experiments as complete; but show promising prospects of important results

Wöhler.

Frederick Wöhler, in Berlin, repeated Oersted's experiment, in 1827, and failed to observe the production of any aluminum, although he remarked that it was not his intention to say that it could not be made that way.[1] Using metallic potassium instead of potassium amalgam, however, he obtained aluminum in the form of a gray powder. Until recently, Wöhler has been generally credited with having been the first one to make aluminum.

About one hundred years later I. Fogh, another Danish scientist, became convinced that Oersted's observations had been reliable, and he repeated Oersted's work.[2] He found it very easy to prepare aluminum by allowing potassium amalgam to react with aluminum chloride. The conditions most favorable for the production of aluminum were the use of a dilute amalgam containing about 1.5 per cent potassium, and the use of an excess of aluminum chloride. The reduced aluminum was dissolved in the mercury and protected in that way from oxidation; the mercury was then driven off by distillation. After Fogh's experiments were complete, Kirstine Meyer[3] discovered certain unpublished notes of Oersted which showed that he was aware of these facts and worked with dilute amalgams and an excess of aluminum chloride.

Something of a controversy has arisen over these developments. The defenders of Wöhler now admit that Oersted made aluminum, but insist that it was quite impure. Oersted's proponents call attention to the fact that Wöhler described his aluminum as a gray powder which did not fuse at the melting point of cast iron! Still others have demonstrated that aluminum can be made by Oersted's method.[4] The honor of first preparing metallic aluminum can be allowed to rest with Oersted without detracting from Wöhler's important contributions to our knowledge of aluminum.

[1] *Pogg. Ann.*, **11**, 146 161 (1827).

[2] Fogh, I., *Det Kgl. Danske Videnskabernes Selskab Mathematiskfysiske Meddeleser*, **3**, No. 14 (1921).

[3] Meyer, Kirstine, "H. C. Oersted, Naturvidenskabelige Skrifter," Kobenhavn, **2**, 465 (1920).

[4] Tosterud, M. and J. D. Edwards, *Trans. Am. Electrochem. Soc.*, **51**, 125 (1927).

In 1845, Wöhler, at the University of Göttingen, succeeded in making aluminum in slightly larger amounts; some of the metallic particles were as large as "big pinheads!"[1] Because of the oxide film on the particles he could not make them coalesce and had to work with these small particles. To Wöhler the world is indebted for the first information as to the properties of this wonderful metal. Wöhler hammered out two metallic globules which together weighed 32 milligrams, and measured their specific gravity; it was 2.50. Three other globules, weighing 34 milligrams, gave a second value of 2.67 for the specific gravity. These figures are very satisfactory, considering the small amount of material available for experimentation; they also constitute the first recognition of the remarkable lightness of this new metal. Working with globules of this size, Wöhler determined that the metal was ductile, stable in air, and melted before the blowpipe. He did not, however, succeed in melting his metallic powder particles together to a coherent metallic mass. A series of observations on the chemical relationship of aluminum to other metals and compounds was recorded by Wöhler.

Sainte-Claire Deville.

Nine years more passed before a third great scientist, H. Sainte-Claire Deville,[2] announced to the French Academy of Sciences, in 1854, an improvement in Wöhler's method of producing aluminum. This discovery inaugurated a period of great experimental activity and marked the beginning of the chemical aluminum industry as contrasted with the present electrochemical industry. As Wöhler changed Oersted's method by leaving out the mercury, so Sainte-Claire Deville changed Wöhler's method by substituting sodium for potassium. He also found that the sodium chloride formed in the reduction of the aluminum chloride made a readily fusible double salt ($NaCl.AlCl_3$) with the excess of aluminum chloride; this salt acted as a flux and allowed the aluminum globules to coalesce. Both changes marked important advances. The substitution of sodium for potassium gave a process with commercial possibilities. The discovery of a flux meant that no longer was it necessary to experiment with particles of aluminum the size of pinheads. The metal was now made in lumps a thousand times greater—say, the size of marbles.

[1] Wöhler, *Liebig's Ann.*, **53**, 422 (1845).

[2] *Comptes rendus* **38**, 279 (1854); **39**, 321 (1854).

It was but a step farther to the production of aluminum in bar and ingot form, and Sainte-Claire Deville's name is closely associated with this development.

Sainte-Claire Deville so aroused the interest and enthusiasm of the members of the French Academy that they contributed 3,000 francs to facilitate research on the production of aluminum.

Fig. 1.   Henri Sainte-Claire Deville.

Later, Emperor Napoleon III became interested in the possibility of using aluminum for helmets and armor, and told Sainte-Claire Deville to continue the experiments on a large scale and at his expense. A number of French scientists and technologists also gave their personal assistance. The experimental work was carried on at the Javel Chemical Works to a point where the process looked practical, even if expensive. Bars of aluminum made at Javel were exhibited at the Paris Exposition in 1855; this was the first introduction of aluminum to the public.

In company with Debray, Morin, and Rousseau Bros., Sainte-Claire Deville began the manufacture of aluminum at Glacière, a suburb of Paris. The neighbors objected to the chlorine and salt fumes, and so the next year, 1857, saw a new plant being installed at Nanterre. The work at Glacière marked commercial progress, for it enabled Sainte-Claire Deville to sell aluminum at 300 francs per kilo ($27 per pound) as compared with 1,000 francs per kilo the year before. At this stage, Sainte-Claire Deville had made about 60 pounds of aluminum altogether.

In 1859, Sainte-Claire Deville published his classic book entitled "De l'Aluminium, ses Propriétés, sa Fabrication et ses Applications." Its 176 pages covered the physical and chemical properties of aluminum, as well as a discussion of its manufacture. Woven through the book is the fascinating story of the birth of the aluminum industry. Near the end of the book is a chapter of 12 pages on the uses of aluminum, which is a brief but brave beginning.

In 1858, the Tissier brothers, Charles and Alexander, published a small book entitled "Recherches sur l'Aluminium," which invited biting sarcasm from the pen of Sainte-Claire Deville. He had befriended these young chemists, and it was in his laboratory they learned much of his experimental work and processes; they made use of this information under circumstances which Sainte-Claire Deville considered quite unfair. Sainte-Claire Deville intimates that he was stimulated into writing his own book in order to prevent his work being misrepresented by the Tissiers.

Sainte-Claire Deville has described the operations at the aluminum works at Nanterre. The double chloride of aluminum and sodium was used in preference to aluminum chloride because it was less deliquescent, less volatile, and easier to handle. Although aluminum-sodium chloride has some fluxing action, Sainte-Claire Deville found that fluorides, such as fluorspar and cryolite, exerted a much greater fluxing action and were more effective in uniting the globules of reduced aluminum. Cryolite was the better flux, but fluorspar was much cheaper. When the price of cryolite was lowered to about $75 per ton, it was substituted for the fluorspar. The following was a typical charge:

	Parts
Aluminum-sodium chloride (crushed)	10
Fluorspar.	5
Sodium (in ingots).	2

This mixture was charged onto the previously heated hearth of a reverberatory furnace. All openings to the furnace were closed to prevent access of air in so far as possible. The reaction, once initiated, proceeded energetically; the mixture was finally heated to ensure completion of the reaction and fusion of the slag. The aluminum was then tapped out of the furnace in a stream and it united into a single body underneath the liquid slag which flowed out last. A small amount of fine aluminum shot usually remained in the slag and this also was recovered by crushing and washing. On a hearth about 1 meter square, 6 to 10 kilos of aluminum were reduced at a time. The price of aluminum had been reduced to 200 francs per kilo (about $17 per pound) in 1859. The average purity of the metal made that year was about 97 per cent.

The principal problem facing the infant industry was the necessity of reducing the cost of production. Enough was known of the properties of aluminum to permit some rosy dreams of its future, if it only could be sold at a reasonable price. The problem was very tantalizing- –alumina was one of the commonest things on earth. Enough to make a pound of aluminum was only worth a few cents, but the aluminum chloride and especially the sodium necessary to reduce it were big items. About three pounds of sodium were required for each pound of aluminum. Sainte-Claire Deville set to work on the problem of producing sodium as early as 1854. The reaction employed was the reduction of sodium carbonate with carbon in the form of charcoal, oil, or coal. Chalk was added to the mixture to prevent fusion of the mass and to maintain a porous reaction mixture. The mixture was placed in an iron container, such as a mercury bottle or an iron cylinder, and heated to reduce and distill the sodium. Sainte-Claire Deville and Tissier brothers improved the details of this process until sodium could be made for about a dollar a pound. No important improvements to the process were made, however, during the next 25 years.

Castner.

Hamilton Y. Castner, of New York, was responsible for the next development in the production of sodium. He, too, was interested in reducing the cost of aluminum On June 1, 1886, Castner was granted a patent[1] covering the reduction of sodium

[1] U. S. Pat. 342,897, June 1, 1886.

hydroxide by means of iron carbide or its equivalent. In this process, finely divided iron was mixed with melted pitch and the mixture coked. It was then crushed, mixed with sodium hydroxide, and heated to about 800°C., at which temperature the sodium is reduced and distills into a condenser. The method was more efficient than prior processes in the utilization of materials and the apparatus cost was less because of longer life. The cost of producing sodium in this way was said to be only about 25 cents per pound.

To make 1 pound of aluminum required 10 pounds of sodium-aluminum chloride. The cost of this compound was by no means a negligible item in the production of aluminum. Its purity was also very important. Any impurity in the chloride, such as iron, was reduced and appeared as impurity in the aluminum. Each 0.1 per cent iron in the salt meant 1 per cent in the aluminum. Aluminum chloride was made by the method discovered by Oersted, which consisted in passing dry chlorine over a heated mixture of alumina and carbon. The double chloride of aluminum and sodium used for the manufacture of aluminum was produced by adding sodium chloride to the reaction mixture of alumina and carbon; at a red heat the double chloride distilled off and was condensed at a temperature of about 200°C.

This process was used, in 1882, by the French company operating the Deville process at Salindres. Aluminum hydrate was first made by calcining bauxite with soda, leaching out sodium aluminate, and precipitating aluminum hydrate by passing carbon dioxide through the solution. The aluminum hydrate was intimately mixed with salt and finely pulverized charcoal, moistened with water, and rolled into lumps the size of oranges. These balls were then placed in retorts and calcined until all moisture was driven off. Then, chlorine was admitted to the retort and the double chloride formed and distilled off.

The first practical application of the Castner sodium process to the production of aluminum by the Deville process was made by the Aluminium Company, Ltd. at Oldbury, near Birmingham, England, where a new works was erected and production started in 1888. During the next year, production reached 500 pounds per day, and the metal was being sold at 16 shillings per pound. This was peak performance for the Deville-Castner process. At about the same time that Castner was inventing

his process of making sodium, another American was inventing a revolutionary process of making aluminum that was to make sodium unnecessary for its reduction. Even though Castner invented another and cheaper process of making sodium by the electrolysis of sodium hydroxide, the Deville-Castner process could not stand the new competition. Castner continued, however, to do a prosperous business in metallic sodium and other related chemicals. His electrolytic process is used today for the manufacture of the world's supply of sodium. In three years' operation he had made some 250,000 pounds of aluminum.
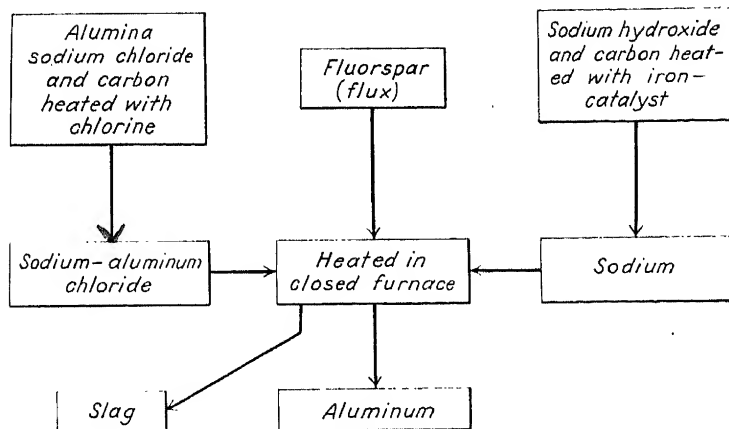
Fig. 2. Diagram of Deville-Castner process.

While the Deville-Castner process represented the most successful development in the production of aluminum by reduction with sodium, other inventors were making and patenting "improvements" by the score. Rose, at Berlin, in 1855, described his experiments on the reduction of cryolite (3NaF.AlF$_3$) with sodium.[1] Percy and Dick were working along the same lines in England, and at almost the same time.[2] Sainte-Claire Deville,[3] likewise, investigated the use of cryolite after learning of the work of Rose and Percy and Dick. The use of cryolite in place of aluminum chloride or the double chloride had the advantage of providing a relatively pure aluminum compound of low volatility. On the other side of the picture

[1] *Pogg. Ann.*, **96**, 152 (1855).
[2] *Phil. Mag.*, Nov. 1855.
[3] *Ann. de Chim. et de Phys.*, (3) **46**, 451 (1856).
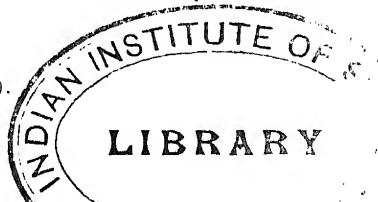
were the facts that it required a higher temperature for reduction, its fluxing action was so strong as readily to take up silica from "earthen crucibles" and contaminate the metal, and furthermore, its supply was at that time uncertain and its cost high. The Tissier brothers reduced cryolite in their plant, working at Amfreville-la-mi-Voie, near Rouen. The plant was not a commercial success, however, and closed down after a few years. Sainte-Claire Deville found that the fluxing properties of cryolite made it a valuable addition agent in his process and used it regularly for that process after it became commercially available. It was also used in combination with the double chloride in the Deville-Castner process as operated at Oldbury, England.

Curt Netto[1] returned to the reduction of cryolite. His process, as carried out near London, involved the melting of a mixture of 100 parts cryolite with 30 to 100 parts of sodium chloride, and then immersing 35 parts of metallic sodium in the molten salt. About 75 per cent of the aluminum in the cryolite was reduced and recovered, which, according to Netto, was twice as good as previous workers had done with cryolite. Netto also developed a process of making sodium in which molten sodium hydroxide was allowed to drip onto a column of red-hot coke and be reduced and volatilized thereby. Netto's processes were used by the Alliance Aluminium Company operating in England.

Ludwig Grabau, of Hanover, Germany, patented a process which employed aluminum fluoride as the source of aluminum, using sodium as the reducing agent.[2] Pure granular aluminum fluoride was heated to about 600°C. and dropped onto molten sodium. The reaction, once started, proceeded energetically without further heating from the outside. The sodium fluoride produced in the reduction formed a fluid slag of sodium aluminum fluoride, under which the aluminum collected. Grabau's process was employed by the Grabau Aluminiumwerke at Trotha, Germany. Many advantages were claimed for the process, among which were an efficient utilization of the sodium (80 to 90 per cent) and the production of very pure aluminum; aluminum of a purity over 99.5 per cent was reported by Grabau. Grabau's process, whatever its merits, came too late. All the sodium reduction processes were shortly to be displaced by a successful electrolytic process which was to make more aluminum in the

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[1] U. S. Pat. 431,912, July 8, 1890.

[2] U. S. Pat. 400,449, Apr. 2, 1889.

first 5 years of its operation than had been made by all other processes together in the preceding 50 years.

Electrolytic Production of Aluminum.

Alumina was one of the substances Sir Humphrey Davy tried to decompose electrolytically. He melted it with current from a powerful battery sufficient to heat iron to a white heat. Apparently some aluminum was reduced, but it alloyed with the iron leads to give a brittle, white alloy. Many years later, Robert Wilhelm Bunsen, at Heidelberg, having succeeded in making magnesium by the electrolysis of fused magnesium chloride,[1] turned his attention to aluminum. By the same method, using fused sodium-aluminum chloride, he prepared aluminum in 1854.[2] The same idea occurred to Sainte-Claire Deville about the same time, and he, also, produced aluminum electrolytically in 1854.[3] Both of these scientists had to obtain their current from batteries. This made the method so expensive that there was little inducement to develop it commercially in competition with the sodium reduction process. Another 25 years was to elapse before dynamo-electric machinery was sufficiently common to be suggested for current supply for electrolysis.

Various inventors tried to find a practical process of electrolyzing the salts of aluminum, but without much success. The double chloride used by Bunsen and Sainte-Claire Deville was very poorly adapted for the purpose. During electrolysis, the aluminum chloride was continually being used up. Aluminum chloride also volatilized from the molten salt, so that the concentration of sodium chloride rapidly increased. This raised the melting point and made it necessary to heat the electrolyte to a higher temperature in order to keep it fluid. Increasing the temperature increased the volatilization losses. The double chloride of aluminum and sodium melts at about 185°C.; because of its volatility it was necessary to electrolyze below the melting point of aluminum. This fact, together with the low fluxing power of the salt, made it very difficult to collect and rescue any aluminum which might be produced. Other difficulties there were, but those just mentioned were sufficient to keep inventors busy.

[1] BUNSEN, *Pogg. Ann.*, **82**, 137 (1852).

[2] BUNSEN, *Pogg. Ann.*, July, 1854.

[3] DEVILLE, *Ann. Chim. Phys.*, **43**, 27 (1854).

Sainte-Claire Deville made one suggestion for the improvement of the process, which was very nice in theory. In order to maintain the aluminum chloride concentration of the electrolyte, he proposed to utilize the chlorine liberated at the anode to make more aluminum chloride. He, therefore, incorporated alumina in the carbon anode on the theory that the chlorine would react with the alumina and carbon to regenerate aluminum chloride. Unfortunately, it didn't work that way in practice. Furthermore, the alumina-carbon electrodes had a very high resistance. Grätzel attempted the commercial operation in Germany of a process employing such electrodes (about 1885). It was a failure.

Other modifications of the process which were suggested were the substitution of cryolite for the double chloride, the use of mixtures of cryolite and sodium chloride, and also aluminum fluoride and sodium chloride. These electrolytes had the advantage of lower volatility, but they still failed to make a commercial process.

Hall.

It remained for an American, Charles Martin Hall, of Oberlin, Ohio, to analyze the problem correctly and successfully solve it. Aluminum oxide could be obtained cheaply and pure; its melting point, 2050°C., however, was a bar to electrolysis in the fused condition. He reasoned that if only he could find a fused salt which would dissolve alumina in substantial quantities, he could electrolyze it in solution. This was an entirely new idea and a different line of attack. He found the solvent in cryolite and, at his home in Oberlin, on Feb. 23, 1886, he electrolyzed a solution of alumina in molten cryolite and produced shining globules of aluminum. Hall's invention consisted of the discovery of a fused electrolyte which would dissolve substantial quantities of alumina and which possessed a higher stability than the alumina, so that the latter could be electrochemically decomposed without affecting the solvent. Hall's electrolyte had the further important advantages of a reasonably low melting point, a low operating voltage of approximately 6 volts, and a specific gravity low enough to permit pure aluminum to sink through the electrolyte and be protected thereby.[1] He devoted himself energetically to the development of his process,

[1] U. S. Pat. 400,766, applied for July 9, 1886, issued Apr. 2, 1889.

and the first works employing it started the production of aluminum in November, 1888, at Pittsburgh. By 1891, the last of the works using the sodium reduction process were closed. With aluminum selling at a dollar a pound, there was no argument as to which was the better process.

Heroult.

Paul L. T. Héroult, of Paris, on Apr. 23, 1886, applied for and was granted a French patent covering the electrolysis of alumina in cryolite, his patent having much the same scope as the Hall process.[1] Héroult also applied for a patent in the United States, but the Patent Office awarded priority of invention to Hall, who had also applied for patent protection. It would appear as if Héroult failed to grasp the possibilities inherent in the alumina-cryolite process, for a year later, Apr. 15, 1887, he took another French patent, as well as a series of foreign patents, on a totally different process which he proceeded to commercialize.[2] His second process only produced aluminum alloys. Pure alumina contained in a carbon-lined crucible or furnace was fused electrothermally by heat from a powerful electric current. A large carbon anode was suspended in the furnace; a layer of molten copper (or iron) in the bottom of the furnace served as cathode and alloyed with the aluminum as it was electrolytically reduced. It was necessary to collect the aluminum in a heavy alloy, because it would otherwise have floated to the top of the heavy fused alumina and burned there. The aluminum bronze alloy could be tapped out of the bottom of the furnace, while copper and alumina were added at the top.

The Société Métallurgique Suisse was formed to acquire both of Héroult's patents and proceeded to erect works at Neuhausen to operate the alloy process. The process was successful and a new company, Aluminium Industrie Aktiengesellschaft, was organized to carry on the process on an enlarged scale at Neuhausen. Dr. Kiliani, a talented electrometallurgical engineer, was made manager of the new enterprise, and a larger factory was put into operation in 1891. The Société Electro-métallurgique Française also built a plant at Froges, France, to make aluminum alloys by the Héroult process.

[1] Fr. Pat. 175,711, Apr. 23, 1886; Br. Pat. 7426 (1887) Apr. 27, 1888.
[2] Fr. Pat. 170,003, Apr. 15, 1887; U. S. Pat. 387,876, Aug. 14, 1888; Ger. Pat. 47,165, Dec. 8, 1887; Br. Pat. 16,853 of 1887, Dec. 7, 1888.

In the meantime, Hall was selling aluminum produced by his process, and on Apr. 2, 1889, his patents issued. With Hall's process in successful operation, Héroult and Kiliani took up the alumina-cryolite process again. They found that the alloy furnaces could be adapted to the production of pure aluminum, and within a few years the alloy process was a thing of the past and their works were making aluminum. Kiliani's name is closely associated with the development of the aluminum industry in Europe.

Several other processes played a passing part. Eugene H. Cowles and Alfred H. Cowles found that a mixture of alumina, carbon, and a heavy metal, such as copper, could be electro-thermally reduced with the production of an aluminum-copper alloy.[1] A heavy current passed through the charge, arranged as a resistor, heated it to a point where alumina was reduced by the carbon. Some less volatile metal, such as copper or iron, was used to absorb the aluminum. Alloys containing up to about 40 per cent aluminum were made in this way, but the average aluminum content was substantially lower.

A service of a different character has been rendered the industry by Dr. Joseph W. Richards, for many years Professor of Metallurgy at Lehigh University, Bethlehem, Pa. When a student at Lehigh, the subject of his thesis was aluminum. His interest in aluminum continued throughout his career, and he was familiar with the industry in a consulting capacity. He soon became a recognized authority on the metallurgy of aluminum and, in 1887, published the first edition of his book, "Aluminium." This was a modest volume of 347 pages. By 1890, a second edition was required, and, in 1896, the third edition appeared with 666 pages. Richards endeavored to collect everything pertaining to aluminum, and to include in his work everything of scientific, practical, or historical value. It therefore affords an invaluable source of information for anyone interested in the industry prior to 1896, and for a long time it was the best and, in fact, the only book on the subject in English. Richards died Oct. 12, 1921, without publishing a fourth edition of his work, which had been expected and was indeed planned by him. The present authors, like many others, have found Richards' book invaluable for reference.

[1] U. S. Pat. 324,658, Aug. 18, 1885.

IMPORTANT DATES IN THE HISTORY OF ALUMINUM

1807. Davy attempts to produce aluminum by electrolyzing fused mixture of alumina and potash.

1825. Oersted produces aluminum by reducing aluminum chloride with potassium amalgam.

1827. Wöhler produces aluminum by reducing aluminum chloride with potassium.

1845. Wöhler makes enough aluminum to determine its density and other important properties.

1854. Sainte-Claire Deville reduces aluminum chloride with sodium and lays the foundation of the aluminum industry.

1854. Bunsen and Sainte-Claire Deville produce the first aluminum by electrolysis, using fused sodium aluminum chloride as electrolyte.

1856. Sainte-Claire Deville, with Debray, Morin, and Rousseau Bros., starts aluminum works at Glacière, France.

1859. Sainte-Claire Deville publishes "De L'Aluminium, ses Propriétés, sa Fabrication et ses Applications."

1885. Cowles brothers produce aluminum alloys by electrothermal reduction of alumina and carbon in the presence of copper, iron, etc.

1886. Castner invents process of producing cheap sodium for reduction of aluminum chloride.

1886. Hall and Héroult invent the first commercially successful electrolytic reduction process and founded the modern aluminum industry.

1888. Pittsburgh Reduction Company (now Aluminum Company of America) was founded.

1888. Aluminium Industrie, A.-G., Neuhausen, Switzerland, founded.

1888. Société Electrométallurgique Française (Froges) starts first electrochemical plant for production of aluminum in France.

1894. The British Aluminium Company founded.

1909. Wilm invents duralumin.

1914. Hall and Héroult die.

1917. Vereinigte Aluminium-Werke, A.-G., formed in Germany.

1919. Hoopes electrolytic refining process perfected.

CHAPTER II

THE STORY OF THE HALL PROCESS

By

JUNIUS D. EDWARDS

Charles Martin Hall.

Any story of the Hall process should begin with Charles Martin Hall, born in the village of Thompson, Geauga County, Ohio, Dec. 6, 1863. While still in college, Hall became engrossed in the problem of finding a new and cheaper method for making aluminum. He was then doing work outside to earn money, and, without neglecting his studies, he carried on his experimental work as well. Having finished his college work, in 1885, he went to Boston for a time, but soon returned to Oberlin and gave his whole attention to a steady, persistent, and finally successful effort to solve the problem he had undertaken.[1]

He was then living in East College Street in Oberlin, with his parents, in a house at the back of which was a large woodshed floored at two levels. Hall put his battery and crucibles along the edge of the upper floor and stood, while at work, on the lower level. In a shed a few feet from the house he had a home-made furnace and bellows. Indeed, all his apparatus was home-made, and he spent days in patient and clever construction of apparatus which he could not afford to buy.

His storeroom for chemicals, alumina, cryolite, and other substances was a room opening from the kitchen. He borrowed or rented some battery jars from the Oberlin College laboratory, fitted them with plates, filled them, and so made a good battery. His crucibles he bought, and one of his early difficulties was caused by silica dissolving from the crucible and contaminating his electrolytes.

Hall seldom became discouraged for more than a few hours at a time. If he met with a difficulty, and there were many, he set himself to devise a method or apparatus to overcome it. He

[1] The story of Hall's early life is based on a short sketch written by his sister, Julia B. Hall, Jan. 20, 1915.

never worked at random, nor did he "stumble onto things." He worked with a clear and definite aim and at twenty-two years of age he had achieved that which many great chemists had failed to do after a half century of work.

Fig. 3.— Charles Martin Hall.

Discovery of Hall Process.

Hall told his family about his work as it progressed, and on Feb. 23, 1886, he called his sisters to show them his first button of aluminum. A bare outline of Hall's process has been given in the preceding chapter. Fortunately, Hall has recorded some interesting details which must not be omitted in telling the story of aluminum.[1]

[1] Remarks by Charles M. Hall upon the presentation to him of the Perkin medal jointly by the Society of Chemical Industry, the American Chemical Society, and the American Electrochemical Society, Jan. 20, 1911.

My first knowledge of chemistry was gained as a schoolboy at Oberlin, Ohio, from reading a book on chemistry which my father studied in college in the 'forties. I still have the book, published in 1841. It is minus the cover and the title page, so I do not know the author. It may be interesting now to see what this book, published seventy years ago, says about aluminum: "The metal may be obtained by heating chloride of aluminum with potassium in a covered platinum or porcelain crucible and dissolving out the salt with water. As thus prepared, it is a gray powder similar to platinum, but when rubbed in a mortar exhibits distinctly metallic lustre. It fuses at a higher temperature than cast iron and in this state is a conductor of electricity but a nonconductor when cold."

Later I read about Deville's work in France, and found the statement that every clay bank was a mine of aluminum and that the metal was as costly as silver. I soon after began to think of processes for making aluminum cheaply. I remember my first experiment was to try to reduce aluminum from clay by means of carbon at a high temperature. I made a mixture of clay with carbon and ignited it in a mixture of charcoal with chlorate of potassium. It is needless to say that no aluminum was produced. I thought of cheapening the chloride of aluminum then used as the basis for aluminum manufacture, and tried to make it by heating chloride of calcium and chloride of magnesium with clay, following the analogy by which iron chloride is produced when common salt is thrown into a porcelain kiln. A little later I worked with pure alumina and tried to find some catalytic agent which would make it possible to reduce alumina with carbon at a high temperature. I tried mixtures of alumina and carbon with barium salts, with cryolite, and with carbonate of soda, hoping to get a double reaction by which the final result would be aluminum. I remember buying some metallic sodium and trying to reduce cryolite, but obtained very poor results. I made some aluminum sulphide, but found it very unpromising as a source of aluminum then, as it has been ever since.

On a later occasion I tried to electrolyze a solution of aluminum salt in water, but found nothing but a deposit of hydroxide on the negative electrode. I did not give a great deal of time to these experiments, as I was then a student in college and was working on three or four other attempted inventions.

I had studied something of thermochemistry, and gradually the idea formed itself in my mind that if I could get a solution of alumina in something which contained no water, and in a solvent which was chemically more stable than the alumina, this would probably give a bath from which aluminum could be obtained by electrolysis.

In February, 1886, I began to experiment on this plan. The first thing in which I tried to dissolve alumina for electrolysis was fluorspar, but I found that its fusing point was too high. I next made some

magnesium fluoride, but found this, also, to have a rather high fusing point. I then took some cryolite, and found that it melted easily and in the molten condition dissolved alumina in large proportions. I rigged up a little electric battery—mostly borrowed from my professor of chemistry, Prof. Jewett, of Oberlin College, where I had graduated the previous summer. I melted some cryolite in a clay crucible and dissolved alumina in it and passed an electric current through the molten mass for about two hours. When I poured out the molten mass I found no aluminum. It then occurred to me that the operation might be interfered with by impurities, principally silica, dissolved from the clay crucible. I next made a carbon crucible and repeated the experiment with better success. After passing the current for about two
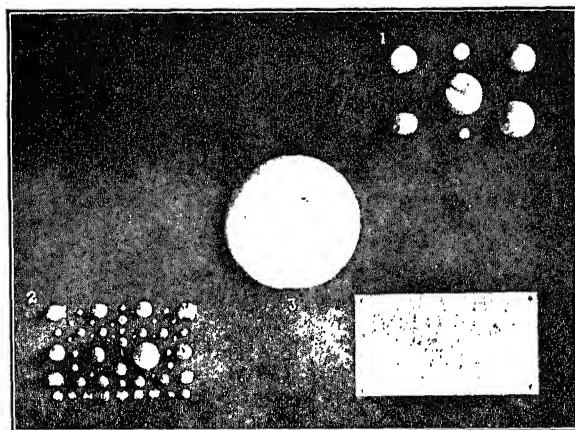
Fig. 4. Photograph of original specimens of aluminum (Nos. 1 and 2 of figure) made by Charles M. Hall with a galvanic battery in 1886 by the process invented by him; the first run or output of aluminum made by the Aluminum Company of America (No. 3 in center of figure).

hours, I poured out the material and found a number of small globules of aluminum. I was then quite sure that I had discovered the process I was after.

I undertook to broaden and improve the method, and found that I could use, instead of cryolite, other double fluorides, particularly a double fluoride of potassium and aluminum. The most important change, however, which I made at this time, was in the material used as anode. I wanted to get rid of the burning up of the carbon anodes. I tried a platinum anode and found that it seemed to work all right, but it was too expensive. I discovered that if I used a fusible bath of a potassium double fluoride, I could use a copper anode, which immediately became coated with a thin film of copper oxide and acted like a permanent platinum anode. This was not a step in advance as I had

hoped, because more or less copper got into the reduced aluminum, and the use of a copper anode led me to use very fusible baths, which on the whole did not work as well as the less fusible baths. It is probable that this change delayed a successful result for a year or two.

When worked on a small scale, this process with any of the baths I have mentioned, and with either copper or carbon anodes, is not apparently promising. The ampere efficiency is low, sometimes zero, and the bath, whether composed of sodium or potassium salt, becomes filled with a black substance which accumulates and renders the process very difficult. In spite of the difficulties mentioned, however, I had great faith in the theoretical possibilities of the process, and believed that the practical obstacles could be overcome, so I stuck to it from the start.

Negotiations with the Cowles Company.

Hall was convinced that the process had great commercial possibilities, but, like many other inventors, he lacked the money to develop it. He therefore sought an opportunity to demonstrate the possibilities to someone able to finance the venture. His first effort, aided by his brother, was in Boston, but the results obtained were unsatisfactory and Hall, disappointed, returned to Oberlin in December, 1886. Six months more were spent in negotiations with a Cleveland chemical manufacturer, who, apparently, was willing to take the process as a gift but would not make Hall a fair offer.

The Cowles Electric Smelting and Aluminum Company, of Cleveland, was at this time making quite a success of the Cowles brothers' aluminum-alloy process. This was a process of electro-thermally reducing alumina in admixture with carbon by passing an electric current through the charge. Because of the high temperature of reduction, it was necessary to collect the reduced aluminum in a less volatile metal, such as copper or iron. Only alloys were produced, and the most valuable was the copper-aluminum alloy with 10 to 20 per cent aluminum, known as "aluminum bronze." The alloys were being sold on the basis of about $5 a pound for the aluminum contained, which was substantially less than pure aluminum was selling for in the market. The Cowles plant was located at Lockport, N. Y. where there was waterpower of 1,200 horsepower available. This constituted the aluminum industry of America at the time.

It seemed logical to join forces with the Cowles Company, so Hall went to Cleveland and on July 26, 1887, entered into an

greement whereby they were to investigate and demonstrate
is process at their Lockport works.   Hall was to receive $75 a
month for his services and, after 90 days, the sum of $750 if they
ecided to continue the investigation.   The Cowles Company
received an option to purchase the Hall process and patents
within six months, for which they were to give Hall one-eighth
nterest (2,500 shares) in the Cowles Company upon its being
recapitalized.

Hall went to work at Lockport.   The course of development
' most new processes is beset with difficulties, particularly where
he work is pioneering in nature, and Hall's process was no
xception.   His work was done on a small scale and without
assistance.   No better picture of the situation can be given than
hat contained in one of Hall's reports.[1]

Lockport, N. Y., Jan. 25, 1888.

Report on Experimental Work

I have now gained a thorough knowledge of the requirements of
my process.   It is now certain that very pure materials will not be
required.   The lack of success for a long time was due to improper
mechanical arrangements and lack of adjustment of the current.

I beg to state that the cost of apparatus and materials has been
small, not over $150 to $200, that I have had the crudest apparatus
and have worked entirely single handed.   In spite of this, the process
now appears to be under control, and I believe the knowledge has
been gained by which to make it a success on any scale.   It appears
that in enlarging the operation no complicated problems will arise,
but that by following a few simple principles success can be easily
attained.   Recently over a pound of pure aluminum has been made.
In order to make it pure and to make it more economically, all that is
required is less crude apparatus.   The prospect now is that the proc-
ess is all that was supposed at the start.   The results of the past six
months' work will appear in the future development of the process.

Respectfully submitted,

Chas. M. Hall.

To the Board of Directors of the Cowles Electric Smelting and
Aluminum Company.

Hall must have been greatly disappointed when he failed
· receive the $750 due at the end of 90 days, because he was

[1] Plaintiff's Exhibit, Cowles Electric Smelting and Aluminum Co., *vs.*
he Pittsburgh Reduction Co., U. S. Circuit Court, Northern District of
w York.

pressed for money to meet the costs of prosecuting his patent applications. For a consideration of $150, however, he extended the time for payment of the $750 and the option period for another 90 days. The Cowles Company again failed to pay the $750 and Hall again extended the time of payment to Apr. 23, 1888. At that time, they told Hall they were no longer interested in his process.

It is difficult to understand why the Cowles Company passed up such a golden opportunity. It is probable, however, that they were so impressed with their own alloy development that they overlooked the possibilities of the new process which had been brought to their door. A short extract from a letter[1] of Edwin Cowles, president of the company, written Aug. 4, 1887, to Mr. Baldwin of the Cowles Company, may explain this attitude:

I think if you understood our reason for making the contract we did with Mr. Hall, you would not have objected to it. The young man submitted his process confidentially to Eugene and Fred, and they both said there was very great possibility of its having great merit, even to the extent of its being able to produce pure aluminum as low as 25 cents per pound. We reasoned as follows: If some parties were to get hold of his process, there might be great danger of its killing our process. As a matter of prudence, we concluded to make some experiments with it. We laid the matter before the Board and they were unanimously of the opinion that it was best that we should make the contract. To be sure, it will cost us a few hundred dollars, but it is a good investment for us on the same principle that we would pay out the same amount to guard against losses by fire. The fact that the young man produced several buttons of aluminum on a kitchen stove alone is sufficient evidence that he might become a great inventor. The price we pay for it will be low if we can produce the pure metal at less than a dollar a pound, for we could, in that case, sell our foreign patents for half again as much, if not double or treble.

Unfortunately for the Cowles Company, they let their agreement lapse and with it their "fire insurance." Hall became convinced that the Cowles brothers wished to discourage him in order to drive a better bargain for his process. He remained at Lockport for a few months longer, continuing his experiments, and paying his own expenses.

[1] Plaintiff's Exhibit, Cowles Electric Smelting and Aluminum Co., *vs.* The Pittsburgh Reduction Co., U. S. Circuit Court, Northern District of New York.

The Pittsburgh Reduction Company.

In July 1888, Hall left Lockport. He knew that establishing his process meant a struggle, but he was more confident than ever. While at Lockport, Hall made the acquaintance of Romaine C. Cole, who shared Hall's enthusiasm for the new process and saw in it a great commercial opportunity. Some years before, Cole had experimented on the reduction of alumina for Alfred E. Hunt, of Pittsburgh, who had formed a partnership with George H. Clapp for testing materials. This was known as Hunt and Clapp, and later, Jan. 1, 1883, was incorporated as The
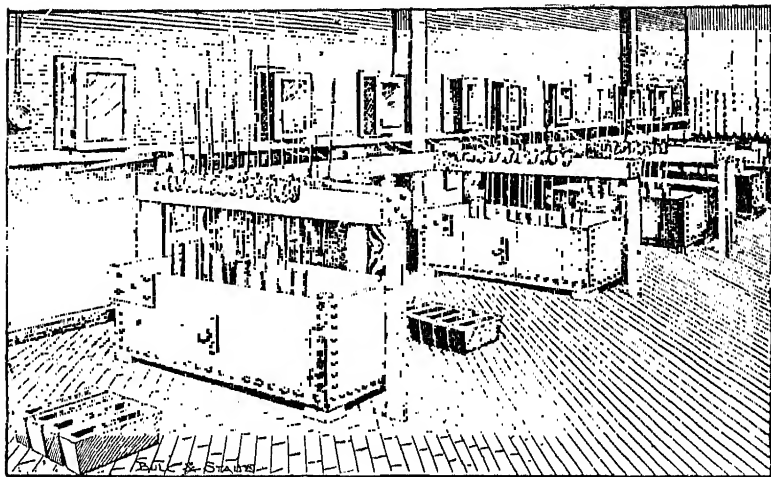
Fig. 5. The Pittsburgh Reduction Company's first cell room.

Pittsburgh Testing Laboratory. When Cole presented Hall's proposition to Hunt, an agreement was quickly effected. Hunt raised $20,000 cash among a few friends and The Pittsburgh Reduction Company was started Sept. 18, 1888. The original subscribers were George H. Clapp, Millard Hunsicker, Alfred E. Hunt, Horace W. Lash, W. S. Sample, and Robert J. Scott.

The first works were installed in a couple of rooms in a building on Smallman Street, Pittsburgh. The electrical equipment consisted of a 125-horsepower steam engine with two dynamos rated at 1,000 amperes each at 25 volts. The first electrolytic cells, or reduction pots, as they are called, were of cast iron, 24

inches long, 16 inches wide, and 20 inches deep, with a 3-inch baked carbon lining. The carbon anodes, 6 to 10 in number, were about 3 inches in diameter and 15 inches long when new; they were suspended by $\frac{3}{8}$-inch copper rods from an overhead copper bus. Each pot held about 200 or 300 pounds of electrolyte or bath, as it is frequently referred to. Two pots were arranged in series and took 1,700 to 1,800 amperes at 16 volts, which was the normal operating voltage. Operating in this way, these pots averaged about 50 pounds of aluminum per day from the time they were started on the night before Thanksgiving, November 1888, until they were scrapped for larger equipment a year or so later.

These first pots were set upon a brick casing so arranged that, if necessary, they could be heated from below by a natural gas flame. It was found, however, that the heating effect of the electric current was sufficient to maintain the bath fluid, and so this external heating was gradually diminished and after a few weeks done away with entirely. Aluminum hydrate was imported from Silesia and calcined at the works to form the anhydrous alumina for charging the pots. The plant was also equipped with a furnace for baking the carbon linings in the reduction pots preparatory to starting them.

Hall was made superintendent, and Hunt appointed another young man, Arthur Vining Davis, then employed by him at the Pittsburgh Testing Laboratory, to alternate with Hall in the day and night management of the work. When the Smallman Street works were ready to start, Hall and Davis were two of the five employees.

A daily production of 50 pounds of aluminum to sell at a profit of several dollars a pound looked very promising to the new company. Although operating on a small scale, its cost of production was less than half that of the best competitive process. Though the Hall process metal at $5 a pound could undersell all other aluminum, there was a very limited market at that price, so the price was reduced to $4 and again to $2 in "half-ton lots" to increase the use of aluminum and stimulate the demand. The rapid reduction in prices did not, at once, greatly increase sales. What was needed was a price low enough to make aluminum attractive for many new uses and, in addition a stable market. With prices falling all the time, many possible users were inclined to wait a while longer and see if prices

wouldn't go lower. When aluminum was offered in half-ton lots, Hall wrote to Cole:[1]

The mention of $2 in 1,000-pound lots didn't seem to interest anyone. I know a good many people look at it as a big guy, and they have reason to do so, as they know that the total consumption of aluminum in the U. S. has hardly been 1,000 pounds a year. People have said we didn't have 1,000 pounds. They were wrong, but they might have said, that so far as the users of aluminum were concerned, practically no one wanted 1,000 pounds.

In spite of the limited demand at first, the company's future seemed assured, and so in the fall of 1889 the capital stock was increased to $1,000,000. Alfred E. Hunt was president and general manager, and Charles M. Hall was vice-president in charge of technical operations. The company was exceptionally fortunate in having a vigorous and able leader of men at its head. Hunt commanded the respect and confidence of his associates, and of Hall. His clear vision and leadership were quite as essential to the ultimate success of the company as was Hall's technical ability.

By the middle of 1890, it was necessary to enlarge the works, and two dynamos having a capacity of 2,500 amperes at 50 volts were installed. The added equipment was in operation by September, giving the company a daily production of about 475 pounds. This plant was used until March, 1891, when its operations were discontinued and a new plant designed for installation on the Allegheny River, at New Kensington, about 19 miles from Pittsburgh.

Litigation with the Cowles Company.

One of the first commercial results of Hall's success was to make it impossible for the Cowles Company to sell aluminum alloys made by their process in competition with those made by alloying Hall's pure aluminum. In order to compete, the Cowles Company secretly adopted Hall's process and started making and selling pure aluminum in January, 1891, in competition with The Pittsburgh Reduction Company. This company imme-

[1] Plaintiff's Exhibit, Cowles Electric Smelting and Aluminum Co., *vs.* The Pittsburgh Reduction Co., U. S. Circuit Court, Northern District of New York.

diately started suit for infringement and the struggle was on in earnest.[1]

The Cowles Company contested the suit energetically. Every possible defence was sought; the art was searched from Davy to Hall for possible anticipations. Expert witnesses testified day after day. The Cowles brothers testified in their own behalf and also brought over Dr. Grätzel from Europe. For The Pittsburgh Reduction Company, Dr. Charles F. Chandler of Columbia University was a resourceful and well-informed witness. The records of the case constitute an excellent history of the art of producing aluminum by electrolysis up to the early 'nineties. The case was argued before Judge Taft (later President Taft) and Judge Ricks, and on motion for rehearing was reargued before Judge Taft. Judge Taft handed down his decision on Jan. 20, 1893, which was a sweeping and clear-cut victory for Hall.[2] The validity of Hall's patent was upheld and the Cowles Company held to have infringed. Judge Taft in his opinion stated:

Hall's process is a new discovery. It is a decided step forward in the art of making aluminum. Since it has been put into practical use, the price of aluminum has been reduced from six or eight dollars a pound to sixty-five cents. This is a revolution in the art and has had the effect of extending the uses of aluminum in many directions not possible when its price was high . . . Hall was a pioneer, and is entitled to the advantages which that fact gives him in the patent law.

The Cowles Company appealed their case, but when the case came up for hearing before the Circuit Court of Appeals, they voluntarily dismissed their own appeal. An injunction was granted and, after a hearing, an award for damages was eventually made to The Pittsburgh Reduction Company.

This litigation was expensive and it consumed the time and attention of the young organization, which had all the problems of this new and complex industry demanding solution. A new menace had been in the making for some time, however, and the company was soon to be involved in further litigation.

One of the points of controversy raised by Cowles in the prior case had been the question of "internal heating of the bath." Hall's original experiments had been on a small scale and he had

[1] A detailed description of the Hall patents and the litigation involving them has been given by Seabury Mastick, *J. Ind. Eng. Chem.*, **7**, 879, 984, 1071 (1915).

[2] 55 *Federal Reporter*, 301.

fused his mixture of cryolite and alumina and kept it molten by heating the crucible in some kind of furnace; that is, by external heating.   This is, of course, almost necessary when working on a small scale.   Hall anticipated that when working on a commercial scale, however, any external source of heat would be unnecessary, and the energy of the electrolyzing current would maintain the bath in a molten state.

On Aug. 29, 1886, he wrote his sister, Miss Julia Hall:

> In some respects this invention is going to be better than I anticipated; thus the resistance of the liquid is exceedingly low.   Also it is evident from the experiments that the waste heat of electricity, which must be used anyway, will be nearly or quite enough to keep the solvent melted.

A similar statement was included in his pending patent specification.   Hall's patent was for a process and not an apparatus, however, and was hence unlimited as to the method of heating employed.   Hall was content to meet the Patent Office requirements by showing one form of apparatus which would work—and he showed the externally heated crucible he had actually employed on a small scale.   Hall considered that the heating of the bath by the current was an inevitable result of passing the current necessary for electrolysis, and that as soon as he operated on a large scale he could not avoid securing the benefits of this internal heat.   It never occurred to him as something that might be patented.

The Bradley Patents.

On Feb. 23, 1883, exactly three years before Hall made his first aluminum, Charles S. Bradley filed a patent application which claimed broadly the idea of fusing "ores" by the electric arc and then passing a current through the ore to decompose it and maintain it in the fused condition.   The decomposition of cryolite as an ore of aluminum was the specific example given by Bradley.   The Patent Office promptly rejected his application on the basis of the prior art.   After the 2 years' period then allowed by the Patent Office, Bradley replied with an amendment. The case dragged on this way for 6 years with one rejection after another.   The principal art relied on by the Patent Office was Davy's preparation of metallic potassium by the electrolysis of potash.   Davy had very definitely stated:

I only attained my object by employing electricity as the common agent for fusion and decomposition.

The Patent Office did not then consider it constituted invention to apply Davy's idea to the electrolysis of cryolite.

A new character appears now, Grosvenor P. Lowrey, who, acting as agent for Bradley, took his patent application in hand. The Hall patents had issued Apr. 2, 1889, and the Hall process was in successful commercial operation. In fact, Lowrey visited The Pittsburgh Reduction Company's plant and viewed the operation of Hall's process. It is obvious from the records that, from this time, the Bradley patent application was being groomed for an assault on the Hall process. After repeated rejection and two appeals to the Examiner-in-Chief, a division of the Bradley application was finally drawn, and limited so as to satisfy the Patent Office Commissioner to whom a final appeal was made. Patents were issued on two similar divisional applications on Dec. 8, 1891, and Feb. 2, 1892.[1]

The Bradley patents were assigned to Grosvenor P. Lowrey, who was interested in introducing the Héroult alloy process into the United States. An experimental plant was erected at Boonton, N. J., under the name of the U. S. Aluminum Metals Company; some experimental work was carried on but it never operated commercially. Bradley and Crocker, who had applied for an electric-furnace patent of interest to the Cowles Company, had made an agreement, in 1885, with the Cowles Company to assign to them any inventions they might make which would "interfere" with the Cowles process. Apparently the Cowles people were not interested in the two particular Bradley patents in question until they issued late in 1891 and early in 1892, since the original Bradley application was known to them but not mentioned in the agreement. The Bradley application referred to an electrolytic process and the Cowles process was strictly electrothermal in character. The Cowles Company now recognized the offensive value of the Bradley patents and laid claim to them under their old contract. Judge Taft heard the suit and on Apr. 23, 1895, awarded title to Lowrey as Bradley's assignee. The case was appealed, however, and the judgement reversed, Feb. 15, 1897.

Just as soon as title to the Bradley patents was transferred, the Cowles Company, now reincorporated as the Electric Smelt-

[1] U. S. Pats. 464,933, Dec. 8, 1891 #468,148, Feb. 2, 1892.

ing and Refining Company, started suit for infringement against The Pittsburgh Reduction Company. Bradley, whose patents were the foundation of the suit, was a bystander in the struggle; his feelings towards the Cowles Company were none too kindly because he felt that he had been unfairly deprived of his patents. This situation probably explains why he was not called as a witness in defense of his patents.

The issues involved might seem to have been fairly simple. Did Bradley discover the art of simultaneously fusing and electrolyzing ores, particularly "refractory ores of aluminum," and was The Pittsburgh Reduction Company practicing his invention as described in his patent claim? As to the matter of discovery, Bradley stated in his proceedings before the Patent Office:

> It is admitted that Sir Humphrey Davy's reduction of potassium and sodium, as described by him, embodied on an infinitesimal scale the process described and claimed by Bradley.

In order to avoid this reference, Bradley limited his claim in a rather indefinite way and made some extravagant representations regarding the pioneering character of his work. The Pittsburgh Reduction Company contended that the Bradley patents, if valid, should be construed narrowly in the light of the limitations placed upon them by the prior art and the Patent Office proceedings. The decision was written by Judge Hazel on Oct. 22, 1901.[1] He did not attempt to pass upon the validity of the Bradley patents but held that, if they were valid, the Hall process did not infringe.

The legal rights were very finely drawn. The question as to who was responsible for the technical and commercial progress made in the production of aluminum is more readily answered. Bradley never operated his process; in fact, it was commercially impractical. The process he disclosed was the simultaneous fusion and electrolysis of cryolite. This was the application of Davy's old method of using the electrolyzing current to maintain fusion of the electrolyte to the old idea of producing aluminum by the electrolysis of cryolite. When this process was tried experimentally, it required continuously from 15 to 50 volts to maintain electrolysis. This was undoubtedly due to the anode effect, of which little was known then. By the time

[1] *111 Federal Reporter,* 742.

Bradley's patent was issued and first made known to the world, the art had long since dispensed with any external source of heat for electrolysis, and this had come as a natural and inevitable development as soon as electrolysis was carried out on a large scale. Bradley was not even sure that fusion could be maintained by the electric current alone, for he described the use of an auxiliary heating device, such as the flame of a blowpipe, directed upon the surface of the electrolyte. This feature is also claimed in another divisional application patented Apr. 26, 1892 (No. 473,866). As a matter of fact, there is no evidence that Bradley's patent was other than a "paper patent."

The Electric Smelting and Refining Company in due course appealed the case, and again the lawyers wrote extensive briefs reviewing the case from every angle. Hall was confident of success. It was a staggering blow, therefore, to have Judge Coxe on Òct. 20, 1903, reverse the decision and hold that the Bradley patents were valid and were infringed.[1] The effect of the decision was to make it impossible for anyone to make aluminum by electrolysis on a commercial scale without infringing the Bradley patents. Furthermore, the holders of the Bradley patents could not make aluminum without infringing the basic Hall patents. The only practical process of making aluminum was by the electrolysis of alumina dissolved in a double-fluoride electrolyte (Hall's process) but the electrolyzing current inevitably kept the electrolyte molten and that act infringed the Bradley patent. The Pittsburgh Reduction Company, however, felt that it had spent enough time and money in litigation and, therefore, effected a settlement with the Electric Smelting and Refining Company whereby it received a license to use the Bradley patents until they expired in 1909.

Development of Aluminum Company of America.

The works at New Kensington were operated by steam power and had a production of 1,000 pounds of aluminum per day in 1893 and 2,000 pounds per day in 1894. At this time, the Niagara Falls power development was inaugurated and the aluminum industry was its first customer. On June 28, 1893, the first power contract calling for 1,500 horsepower, with an option on 1,000 horsepower additional, was made with the Niagara Falls Power Company. A new reduction works was designed, con-

[1] *125 Federal Reporter*, 926.
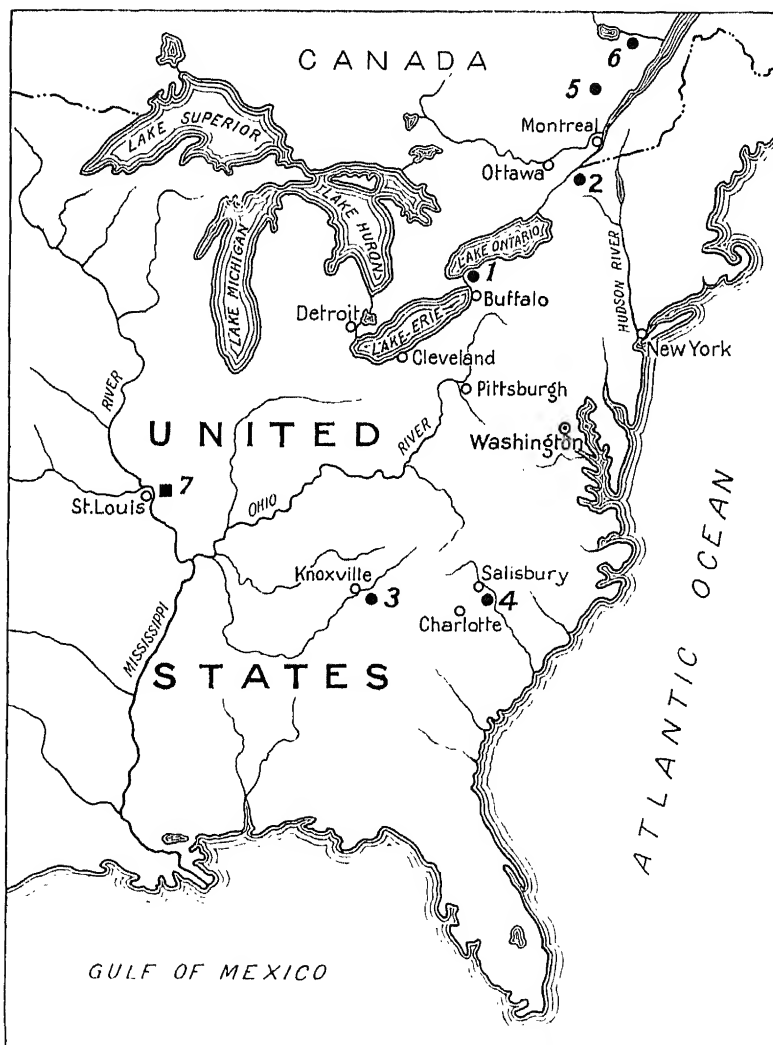
Fig. 6. Location in United States and Canada of aluminum reduction works (●) and alumina works (■).

Aluminum Reduction Works

Aluminum Company of America Pittsburgh, Pennsylvania	1. Niagara Falls, New York 2. Massena, New York 3. Alcoa, Tennessee
Tallassee Power Company (Owned by Aluminum Company of America)	4. Badin, North Carolina
Aluminum Company of Canada (Owned by Aluminium Limited)	5. Shawinigan, Quebec 6. Arvida, Quebec

Alumina Works

Aluminum Ore Company (Owned by Aluminum Company of America)	7 East St. Louis, Illinois

structed, and put into operation on Aug. 26, 1895. The following year, on Nov. 21, a second works was started. In succeeding years, additions were made to the Niagara works and the production of aluminum greatly expanded. With increasing industrial development in the Niagara Falls district, and increased power costs, the aluminum industry turned towards cheaper power for its next requirements. The first two works constructed at Niagara have been abandoned and only a third, the most modern plant, is being continued in operation at the present time.

Charles M. Hall died Dec. 27, 1914, at Daytona, Fla. His alma mater, Oberlin College, was the recipient of a generous bequest from his estate, as was also Berea College, in which he was interested. In fact, Mr. Hall bequeathed the greater part of the considerable fortune his patents and business acumen had brought him to the cause of education. Capt. Alfred E. Hunt, the first president of the company, died Apr. 26, 1899. He was succeeded by Arthur Vining Davis, who since then has guided the destinies of the Company. In June, 1928, he became Chairman of the Board and Roy A. Hunt, son of Alfred E. Hunt, became president of the Aluminum Company of America. Another of the pioneers of the aluminum industry was William Hoopes, Chief Electrical Engineer of the Aluminum Company of America, who died Jan. 9, 1924. Mr. Hoopes developed the use of aluminum for the transmission of electric power, and its rapid adoption and widespread use for this purpose is largely due to his ingenuity and inventiveness.

On Jan. 1, 1907, The Pittsburgh Reduction Company changed its name to Aluminum Company of America. With the growth of the company, additional reduction works were constructed at Massena, N. Y., where power is generated from water from the St. Lawrence River; at Badin, N. C., in connection with a power development on the Yadkin River, and at Alcoa, Tenn., where power is secured from a series of developments, some of which are still in course of construction on the Little Tennessee River in the Great Smoky Mountains. In Canada, a plant was built in 1901 at Shawinigan Falls, P. Q., on the St. Maurice River, and a new project was started in 1926 on the Saguenay River, at Arvida, P. Q.

Aluminium Limited.

In 1928, the foreign holdings and interests of the Aluminum Company of America had become so extensive as to require a

separate organization for their proper development. Accordingly, Aluminium Limited, a Canadian corporation, was formed and acquired the various properties of the Aluminum Company of America, outside of the United States. Edward K. Davis is president of Aluminium Limited. The principal reduction works of Aluminium Limited are in Canada, Norway, and Italy. In Canada, the operations are under the Aluminum Company of Canada, Limited; in Norway, the operating companies are the Norsk Aluminium Company and Det Norske Nitridaktieselskab, and in Italy, Alluminio Italiano.

The Arvida works of Aluminum Company of Canada, Limited are located close to the remarkable power developments[1] on the Saguenay River, the outlet of Lake St. John, which forms a natural storage basin with an area of 400 square miles and receives the run-off of over 30,000 square miles. It is estimated that it will store and make available some 200,000,000,000 cubic feet of water. At the present time, about 500,000 horsepower is being developed at Isle Maligne and additional developments are under construction that will bring the total to over 1,000,000 horsepower. Arvida is 24 miles from and connected by rail with Port Alfred, P. Q. Wharves are available for the largest ocean-going vessels. Cheap power and transportation were important factors in drawing the industry to this locality.

[1] McBride has described this plant in *Chem. Met. Eng.*, **33**, 724, December, 1926; **34**, 76, February, 1927.

CHAPTER III

THE ALUMINUM INDUSTRY IN EUROPE

By

Junius D. Edwards

FRANCE

To France belongs the honor of having founded the aluminum industry through the work of Henri Sainte-Claire Deville. Later, when the chemical process was succeeded by the electrochemical process, another Frenchman, Paul Héroult, shared with Charles M. Hall the honor of discovering the successful process. Furthermore, the usual ore from which aluminum is made, bauxite, takes its name from Les Baux, a small and ancient Provençal village, where it was first discovered. The history of the industry in France has, therefore, been of great significance.[1]

Henri Sainte-Claire Deville was born Mar. 18, 1818, at St. Thomas in the West Indies. After his father's death, he went to France with his brother, Charles, and studied first at Sainte-Barbe and then at Rollin College. Both brothers were interested in science and achieved fame in that line of endeavor. In 1843, Henri Sainte-Claire Deville received the degree of Doctor of Medicine and Doctor of Science. The next year, at the age of twenty-six Sainte-Claire Deville became Dean of Besançon University where he also taught chemistry. In 1851, he occupied the chair of chemistry at the École Normale Supérieure. It was in the laboratories of this school that most of his important discoveries were made. Shortly after, in 1854 Sainte-Claire Deville made the first announcement of his work on aluminum. By substituting sodium for potassium in the reaction with aluminum chloride, Sainte-Claire Deville made a big advance in lowering the cost of producing the metal, and by substituting the double chloride of sodium and aluminum he made it possible

[1] The author is indebted to Louis Marlio of L'Aluminium Français for much of the information about the French aluminum industry.

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to melt and collect the reduced aluminum in the form of solid ingots. The world at large had its first view of aluminum at the Paris Exposition of 1855, where Sainte-Claire Deville exhibited bars of aluminum made by his process. These bars were exhibited in such a way that visitors could lift them and marvel at their lightness. At this stage, aluminum looked like a competitor of silver, and it did not go unnoticed that the aluminum exhibit was close by that of the crown jewels. Sainte-Claire Deville followed closely the industrial exploitation of his process and in his book, "De l'Aluminium," gave to the world the first comprehensive treatise on aluminum. Sainte-Claire Deville was appointed a member of the Institute in 1861. He died in 1881 with no competitor of his process in sight.

Paul Louis Toussaint Héroult was of the next generation, born, in 1863, at Thury-Harcourt in the Calvados district. During the war of 1870, Paul Héroult stayed with his grandfather in London and became familiar with the English language in this way. Three years later he returned to France to continue his studies. Héroult also attended Sainte-Barbe college and exhibited an early interest in natural science, physics, chemistry, and mechanics. At the age of fifteen he had the opportunity of reading Deville's book on aluminum. His interest in aluminum seems to have begun at that time. His interest took definite form when his father's death, in 1885, left him with a small tannery at Gentilly. The tannery was provided with a steam engine, and with the addition of a small Gramme dynamo, Héroult was equipped to experiment with the electrolysis of the various compounds of aluminum. After many efforts, Héroult's experiments were crowned with success.[1] Later, in 1900, Héroult described the discovery of his process as follows:

Convinced that it was possible to produce aluminum by electrolysis, after numerous failures with aqueous solutions, I tried to decompose the fused halide salts by means of the electric current.

It must be remembered that, at that time, the electrical industry was in its infancy. The biggest carbons one could secure were less than 50 mm. in diameter. The few crucibles available in the laboratories were made by turning and hollowing out a piece of retort carbon. After numerous failures, I was much encouraged when, during an effort to electrolyze cryolite, the iron cathode melted and allowed the contents of the crucible to escape. The temperature at which I was operating

[1] Fr. Pat. 175,711, Apr. 23, 1886.

and the few Bunsen elements I used at that time were not sufficient to explain the melting of the iron. From an examination of the remains of the cathode, it seemed probable that an alloy had been formed. A few days later, having tried to lower the temperature of the electrolyte by mixing the double chloride of sodium and aluminum with it, I was

FIG. 7.—Paul Louis Toussaint Heroult.

surprised to find that the carbon anode showed obvious signs of attack. I concluded that I was dealing with an oxide whose reduction was effected at the expense of the anode. After investigation, I found that what I had bought for double chloride was, in reality, alumina resulting from the decomposition of the chloride by moisture. From this it was but a step to discover the present process used for the manufacture of aluminum. This was, nevertheless, difficult to accomplish and the

detailed story of the period which followed would be tedious to hear. My knowledge of chemistry was limited to what a twenty-three-year old student, who had not specialized, could acquire. In view of this fact, it is not surprising that, my first patent having been secured, I sought aid from among those who were authorities on the subject. One of those whom I consulted said, "Aluminum is a metal with limited markets and should you sell it for 10 francs or 100 francs per kilo, you would not sell one more kilo. Should you make aluminum bronze, that would be a different matter, for substantial quantities of the latter are used."

I made some encouraging experiments along that line. I laid aside the production of pure aluminum for a new series of experiments which led in 1887 to an addition to my first patent. This addition described an electric furnace and process for the continuous production of aluminum alloys by electricity and in general for the production of substances difficult to melt or reduce.

Héroult, with the aid of friends, continued his experimental work at Gentilly. He now had a dynamo built by Breguet for a current of 400 amperes at 30 volts, which was a very powerful machine for that time, and by its use Héroult was able to experiment on a much larger scale. However, Héroult was not able to secure in France the support necessary for the commercial exploitation of his process, and in 1887 he went to Switzerland, where he opened negotiations with Naville and Hüber. This led to the founding of the company, Aluminium Industrie, at Neuhausen. They first undertook the commercialization of Héroult's alloy process, which involved the electrolysis of fused alumina in the presence of a cathode of molten copper, with the production of an aluminum-copper alloy, aluminum bronze. Several years later, with the cooperation of Kiliani, the production of pure aluminum was begun at Neuhausen.

The success of the Héroult process at Neuhausen attracted the attention of French capitalists and led to the founding of the first French company for the operation of the Héroult process. This company was named Société Electrométallurgique Française, or as it was commonly known, Société de Froges, taking its name from the first hydro-electric plant built by this company at Froges in the Isère Valley, near Grenoble.

In May, 1889, Héroult came to the United States with the idea of starting operation of his alloy process. Experimental work was undertaken at Bridgeport, Conn., but owing to a short circuit which burned out the only available dynamo, it

became necessary to discontinue the work and it was not later resumed.   Upon his return to France, Héroult devoted all his energies to the commercialization of his process at the Froges works and later, in 1893, he was interested in the construction of the Praz works.   At the Praz hydro-electric plant it became necessary to cross the River Arc with a large penstock carrying water to the turbines.   Héroult conceived the idea of building the penstock in the form of an arch over the river without any additional supporting structure.   This was a daring piece of engineering at that time, but it proved sound in theory and practice and has since become common practice.

Héroult did not confine his genius to the aluminum industry, but beginning in 1900 devoted much of his time to the electro-metallurgy of iron and steel.   He made frequent trips abroad and seemed particularly at home in America, where his command of the English language stood him in good stead.   He was directly interested in the Badin aluminum works which the Southern Aluminum Company started at Whitney, N. C. Héroult died in 1914, only three months before the outbreak of the World War.   It is of interest to note that both Hall and Héroult were twenty-three years old at the time they discovered the Hall-Héroult process of producing aluminum.

There are now only two companies producing aluminum in France, but they have resulted from the combination and merging of a number of companies which have had an interesting history.   The first of these companies is known as Cie de Produits Chimiques et Electrométallurgiques Alais, Froges et Camargue, or as it is sometimes briefly called, "Compagnie A. F. C."   Its history dates back to January, 1885, when Henry Merle founded the joint stock company, "Henry Merle et Cie," for the production of soda and other chemical products at Salindres, not far from the town of Alais or Alés (Department of Gard).   This field of activity was soon enlarged and a source of salt was acquired in the salt pools of the Camargue.   When the company was reorganized in 1855, it took the name, "Cie de Produits Chimiques d'Alais et de la Camargue," sometimes abbreviated as "Compagnie Alais."   The progressive policies of Henry Merle brought to the company the assistance of such well-known men as Balard, J. B. Dumas, Walter Weldon, Sir James Dewar, Prof. Lunge, of Zurich, and Henri Sainte-Claire Deville.

It was with the cooperation of Sainte-Claire Deville that the Salindres plant was equipped for the first real industrial reduction of aluminum by the chemical method. Production on a small scale was maintained here for more than 30 years—until the electrochemical process took the field in 1889. In 1887, M. Péchiney became managing director, and it was under his management that the Minet electrochemical works at Calypso were acquired. In 1906, the St. Jean de Maurienne works were erected and were completed in 1912 by the addition of the Pontamafrey power house. In 1914, the companies' production was increased by merger with the Société des Produits Electrochimiques et Métallurgiques des Pyrénées, and, in 1916, by Société des Forces Motrices et Usines de l'Arve.

The Société des Forces Motrices et Usines de l'Arve was founded in 1895 and developed its first hydro-electric power at the Chedde fall on the Arve river. The power was first employed in the manufacture of alkali chlorates and it was not until 1906 that the production of aluminum was undertaken. In 1916, it was merged with the Compagnie Alais, as just mentioned.

The Société des Produits Electrochimiques et Métallurgiques des Pyrénées was founded in 1906 by the same group as the preceding company. The power came from a 400-meter fall at Auzat in the Ariège department and aluminum was produced from the start. In 1914, the Auzat works were also purchased by Compagnie Alais.

At this point, the story must go back to the founding of Société Electrométallurgique Française (Froges) in 1888. This company purchased the French patents for the Héroult process from Aluminium Industrie, Neuhausen, and prepared to start the electrochemical production of aluminum in France. The first installation was made at Froges in the Isère Department, and this was the first electrometallurgical plant in France. Soon the available energy, which was only a few hundred horsepower, became insufficient for their needs and they began to look for additional power in the high valleys of the Alps. The next installation was at La Praz on the Arc river, near Modane (Savoie). At about the same time, the alumina works at Gardanne (Bouches-du-Rhône) was purchased. It is of interest to note that Héroult carried out his work on the electrometallurgy of steel at the La Praz plant. In 1903, another plant was built at La Saussaz, St. Michel du Maurienne. Again, in 1910, the largest and
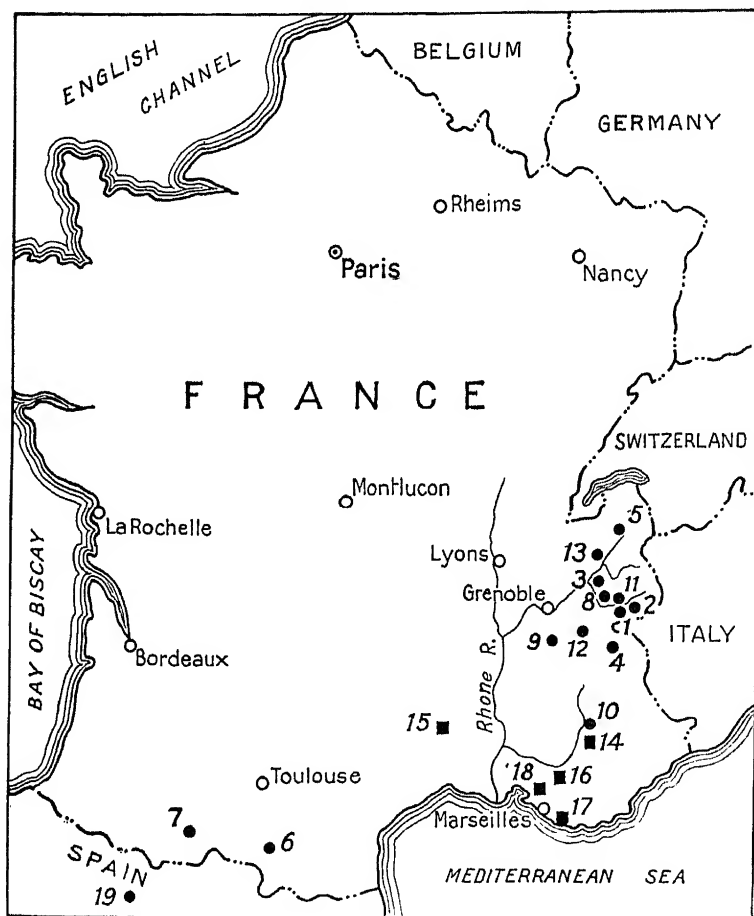
Fig. 8.—Location in France and Spain of aluminum reduction works (●) and alumina works (■).

Aluminum Reduction Works

Compagnie de Produits Chimiques et Electrométallurgiques Alais, Froges et Camargue

1. La Praz, (Savoie), France
2. Calypso, (Savoie)
3. St. Jean de Maurienne, (Savoie)
4. L'Argentière-la-Bassée, (Hautes-Alpes)
5. Chedde, (Haute-Savoie)
6. Auzat (Ariège)
7. Beyrède, (Hautes-Pyrénés)
8. La Saussaz at St. Michel de Maurienne

Société d'Electrochimie, d'Electrométallurgie et des Aciéries Electriques d'Ugine

9. Rioupéroux, (Isère)
10. St. Auban, (Basses-Alpes)
11. Prémont St. Michel, (St. Michel de Maurienne-Savoie on the Arc)
12. Les Clavaux, (Isère, on the Romanche)
13. Venthon, (Haute-Savoie)

Aluminio Español, S. A.
(Owned by Compagnie A. F. C. and Aluminium Industrie, A.-G.)

19. Sabañanigo, (Huesca), Spain

most important aluminum producing works in France were erected at l'Argentière (Hautes-Alpes) on the Durance river.

In 1921, the Compagnie des Produits Chimiques d'Alais et de la Camargue, whose history has already been described, merged with the Société Electrométallurgique Française and the new company became known as "Compagnie des Produits Chimiques et Electrométallurgiques Alais, Froges et Camargue," or, to abbreviate, "Compagnie A. F. C." At the present time, this company, together with the Société d'Electrochimie, d'Electrométallurgie et des Aciéries Electriques d'Ugine, are the only producers of aluminum in France. Since the World War, Compagnie A. F. C. has made every effort to modernize their extensive plants and acquire new production. In 1924, in agreement with the Société d'Electrochimie, aluminum works were installed at Beyrède (Pyrénées) on the Neste river. In 1925, the Rioupéroux works on the Romanche river was secured by lease and aluminum reduction works installed the next year. During 1926, the Saint Auban works were being built for the production of aluminum. Power for this works will be secured from the Poët fall on the Durance river. Additional hydro-electric works are being installed in the Pyrénées at Sabart falls, and at the falls of Bonne et Drac in the Alps, as well as the St. Guilherme fall on the Romanche river.

The Société d'Electrochimie, d'Electrométallurgie et des Aciéries Electriques d'Ugine is the other organization producing aluminum in France and, like Compagnie A. F. C., was formed by the merging and absorption of several different companies. The Société d'Electrochimie was formed on Aug. 2, 1889, for the purpose of producing and selling chlorates and other electro-chemical products. The successive combination of the Société d'Electrochimie, la Volta, Société des Carbures Métalliques, Société Electrométallurgique du Giffre, and, in 1922, the merging with the Aciéries Electriques Paul Girod d'Ugine, have resulted in the formation of the present Société d'Electrochimie, d'Electrométallurgie et des Aciéries Electriques d'Ugine. This com-

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Alumina Works

Compagnie de Produits Chimiques et Electrométallurgiques Alais, Froges et Camargue
Société d'Electrochimie, d'Electrometallurgie et des Aciéries Electriques d'Ugine
Société Française pour L'Industrie de L'Aluminium
(Owned by Aluminium Industrie, A. G.)

14. St Auban, (Basses-Alpes), France
15. Salindres, (Gard)
16. Gardanne (Bouches-du-Rhône)
17. La Barasse, (Bouches-du-Rhône)

18. St. Louis les Aygaylades, (Bouches-du-Rhône)

pany possesses a number of hydro-electric plants, which for the most part are located in the French Alps in the Isère, Arc, Arly, and Romanche valleys, and it is engaged in general electro-chemical, electrothermic, and electrometallurgical operations in 18 large works which secure their power from 23 power houses. Aluminum is produced at Premont, Les Clavaux, and Venthon. Alumina is secured from the works at La Barasse.

In addition to the producing companies in France, whose histories have just been outlined, there is a selling organization known as "L'Aluminium Français," founded in 1911, which represents Compagnie A. F. C. and the Société d'Electrochimie, d'Electrométallurgie d'Ugine. In addition to being the selling branch for both producing organizations, L'Aluminium Français is also engaged in the fabrication of aluminum and light alloys in wrought forms, such as rolled sheet, wire bars, plates, tubing, and molding, and carries on in its laboratories investigations on the uses and industrial applications of aluminum and its alloys.

The "Aluminium du Sud-Ouest" was formed in 1906 with the object of manufacturing aluminum, and built a power plant at Beyrède on the River Neste. At the present time, the power is sold to Compagnie A. F. C. and, with power from another plant, is used in the production of aluminum at the Beyrède works. The majority of this company's stock is now owned by L'Aluminium Français.

Electro-Métallurgie du Sud-Est was formed in 1906 for the manufacture of a'uminum and built a plant at Venthon (Savoy district) for this purpose. This company was a subsidiary of Aluminium du Sud-Ouest. The plant was later sold to the Société Paul Girod, and belongs at present to the Société d'Electrochimie, d'Electrométallurgie et des Aciéries Electriques d'Ugine, which is going to make aluminum there.

In addition to its French production, Compagnie A. F. C. is interested in Det Norske Nitridaktieselskab, with works at Eydehavn and Tyssedal, Norway.

It would not do to leave the history of the French aluminum industry without saying something about Adrien Badin, who was so intimately identified with its progress. Adrien Badin, born in 1873, graduated from the École des Mines de St. Etienne. After seven years' experience as a professor at École des Maîtres Mineurs d'Alais, he became engineer at the Salindres works and was chosen by M. Péchiney as his assistant. He took an active

part in the business affairs of Compagnie Alais and when M. Péchiney retired, in 1907, Badin was appointed general manager, a position which he held until 1914, when he became a member of the board and managing director.

Few branches of the industry remained unfamiliar to Badin, but most of his time and energy were given to the aluminum industry. With keen foresight he discerned its great future and, with bold confidence, led his company ahead. Under the leadership of Badin, the company constantly increased its facilities. As early as 1902 the plant of St. Félix was purchased, and he undertook the equipment of the works at the Calypso fall, which were completed in 1905. In 1907, the important St. Jean de Maurienne works were put in operation, their power requirements being completed in 1912 by the hydro-electric plant at Pontamafrey. As soon as the works were complete, Badin began negotiations resulting in the merger of the Société Electrochimique et Electrométallurgique des Pyrénées and of the Société des Forces Motrices et Usines de l'Arve, bringing into his organization the Auzat, Chedde and Epierre plants.

Badin's creative activity did not stop with the rapid expansion of the French producing works, but he conceived the extensive works of the Southern Aluminum Company, the construction of which was started near Whitney, N. C., in 1914. The outbreak of the World War prevented the carrying out of his plans, however, and the company's holdings were sold to Aluminum Company of America in 1915. The town built in connection with this works was named Badin — a tribute to the man who established it. During the World War and until he died in 1917, Badin devoted all of his energies toward increasing the French production of necessary war materials.

GREAT BRITAIN

Sir Humphrey Davy, as early as 1807, carried out a series of experiments designed to separate the metallic base of alumina.[1] The electrolytic method he had so successfully employed in the preparation of sodium and potassium did not yield metallic aluminum in a form which he could isolate and identify. The first specimen of aluminum produced in England was exhib-

[1] The author is indebted to W. Murray Morrison of The British Aluminium Company for much of the information about the aluminum industry in Great Britain.

ited by Dick and Smith on Mar. 30, 1855, at one of the Friday evening meetings of the Royal Institution. Working under the supervision of Dr. Percy, they showed that aluminum could be produced by reducing cryolite with metallic sodium.

The first commercial production of aluminum in England was undertaken by F. W. Gerhard at Battersea, London, where the Deville process was employed. These works were closed about 1863. With the coöperation of Sainte-Claire Deville, Bell Brothers established an aluminum works at Washington, near Newcastle-on-Tyne, England. Aluminum was produced here from 1860 to 1874. The Deville process was operated with increasing success in England until displaced by the Hall-Héroult electrolytic process. The Deville process reached its highest development and made its last stand in England.

The Aluminium Crown Metal Company of Birmingham, England, operated the Deville process in 1881 and 1882. They held the rights to a new process of James Webster for the production of aluminum chloride, but it is not clear how successful it was. Nevertheless, this company was merged with the Aluminium Company, Limited, in 1887 and plans made to produce aluminum with the aid of cheap sodium produced by Castner's process. A plant was constructed at Oldbury, near Birmingham, and operations were started in July, 1888. In 3 years' operation some 250,000 pounds of aluminum were produced and the price reduced to 15 shillings per pound. The development of the electrolytic process was so rapid, however, that by 1891 the Oldbury works ceased operations.

The modern aluminum industry in Great Britain dates from the formation of The British Aluminium Company, Limited, on May 7, 1894. Prior to this, aluminum was made at the works of the Cowles Syndicate at Milton, Stoke-on-Trent, Staffordshire, England, beginning in 1890, but the works closed in 1893. Works were also started in July, 1890, at Patricoft, Lancashire, to operate Hall's electrolytic process, but this plant also ceased operations in 1894. The Héroult patent covering the electrolysis of alumina in fused cryolite was granted Apr. 27, 1888, in Great Britain.[1] The British Aluminium Company acquired the British and Colonial rights to the Héroult patents from the Société Anonyme pour l'Industrie de l'Aluminium, Neuhausen, Switzerland. The British Company also purchased the patents of

[1] Patent 7,426 (1887) granted Apr. 27, 1888.
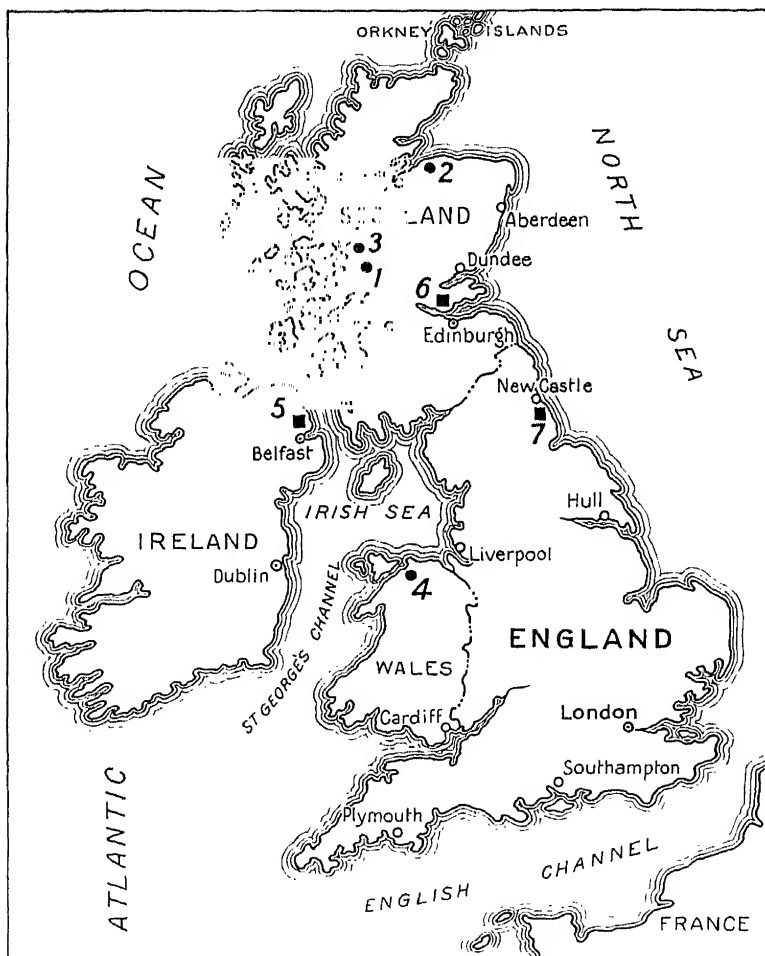
Fig. 9.   Location in Great Britain of aluminum reduction works (●) and alumina works (■).

Aluminum Reduction Works

British Aluminium Company, Ltd

North British Aluminium Co., Ltd
  (Owned by British Aluminium Co., Ltd.)
Aluminium Corporation, Ltd

1. Kinlochleven, Argyllshire, Scotland
2. Foyers, Inverness-shire, Scotland
3. Fort William, Inverness-shire, Scotland

4. Dolgarrog Sidings, near Llanwrst, North Wales

Alumina Works

British Aluminium Company, Ltd.

International Aluminium Co., Ltd.
  (Owned by Aluminium Corporation, Ltd.)

5. Larne Harbour, County Antrim, Ireland
6. Burnt Island, Fifeshire, Scotland
7. Hebburn, Newcastle-on-Tyne, England

K. J. Bayer for the production of alumina. With possession of the Héroult and Bayer patents, The British Aluminium Company clearly dominated the situation in Great Britain.

The first works built by the British Aluminium Company used hydro-electric power and were located at Foyers, Inverness-Shire, Scotland, and the production of aluminum was started there in June, 1896. The next hydro-electric development of this company was at Kinlochleven, Argyllshire, Scotland. The production of aluminum was started in a temporary factory in December, 1907, and a permanent plant was put into operation in February, 1909.

With cheap electric power a prime consideration in the production of aluminum, the British Aluminium Company next turned its attention to Norway. Near the end of 1907, the British Aluminium Company acquired a partly developed water-power project at Stangfjord on the west coast of Norway, about one hundred miles north of Bergen, through purchase of the Aktie-selskapet Stangfjordens Elektrokemiske Fabriker. Production of aluminum was started at this plant in January, 1908. Additional production was secured in July, 1912, through purchase of another Norwegian company named Aktieselskapet Vigelands Brug with works at Vigelands, near Kristianssand, South Norway. In January, 1923, the British Company still further increased their Norwegian production by acquiring a one-third interest in Det Norske Nitrid, A./S.

At the present time, the British Aluminium Company is enlarging its operations in Scotland. A large waterpower development was acquired in 1921 at Lochaber, Inverness-Shire, Scotland. The hydro-electric development is now in course of construction by a subsidiary named Lochaber Power Company and, when completed, the production of aluminum will be carried out at Fort William by another subsidiary, The North British Aluminium Company, Limited.

The British Aluminium Company's first alumina plant was put into operation in the spring of 1896 at Larne Harbour, County Antrim, Ireland. The company had acquired extensive bauxite deposits in County Antrim and it was planned to use this ore for the production of alumina. After several months' operation, however, its quality was found to be such that it was uneconomical to continue its use and, beginning in 1897, French bauxite was imported. In 1913, a second alumina works was

started at Burnt Island, Fifeshire, Scotland. Owing to the delays occasioned by the World War, it was not until October, 1917, that this plant reached the production stage.

Carbon electrodes were produced at a plant in Greenock, Scotland, from 1896 until 1910. Production was then carried on at a new carbon electrode plant at Kinlochleven, Argyllshire, Scotland.

In April, 1907, another British company, the Aluminium Corporation, Limited, was founded for the purpose of producing aluminum in North Wales. In order to secure production as quickly as possible, temporary works using steam power were erected by the corporation at Wallsend-on-Tyne, England. When the company's works were completed and put into operation at Dolgarrog, North Wales, towards the end of 1908, operations were discontinued at Wallsend-on-Tyne. After only 2 months' operation, the company met with financial difficulties and operations ceased. At the beginning of 1910, the company was reorganized and the Dolgarrog works reopened and have continued production on a small scale to date. The Aluminium Corporation secures its alumina from a plant at Hebburn-on-Tyne, England, The International Aluminium Company, Limited. The Aluminium Corporation is also producing aluminum at Glomfjord, Norway, by its subsidiary, A/S Haugvik Smelteverk.

GERMANY

The aluminum industry owes much to the efforts of German scientists, notably Wöhler and Bunsen.[1] It was only recently, however, that any substantial production of aluminum has been undertaken in Germany. Aluminium Industrie, A.-G., Neuhausen, constructed a small plant at Rheinfelden, Germany, in 1897, but its yearly production of about 800 metric tons was only a fraction of the annual domestic requirement. The statistical position of aluminum, as well as lack of cheap electric power, did not encourage any effort to start domestic production. The outbreak of the World War in 1914 changed the situation almost over night. Shut off from the rest of the world, Germany was faced with the problem of producing an adequate supply

[1] The author is indebted to Ernst Rauch of Vereinigte Aluminium-Werke A.-G. for much of the information about the German aluminum industry.

of aluminum within its own borders. Aluminum was needed, not only for extensive military applications, but likewise for domestic uses. The available supply of copper was strictly limited and aluminum came to be used in its place wherever possible.

The Chemische Fabrik Griesheim Elektron in association with Metallbank und Metallurgische Gesellschaft undertook the construction of three aluminum reduction works which were to have an annual capacity of 6,000 metric tons of aluminum.

The first of these reduction works was constructed at Rummelsburg, near Berlin, and was put into operation in December, 1915. Current was obtained from a near-by steam power plant already in operation. The Rummelsburg works was only designed as a war plant; however, it not only produced the 300 tons per month for which it was planned, but some 15 to 20 per cent more. At the close of the war, the Rummelsburg works were closed and dismantled.

The second plant was started at Horrem in January, 1916, with power from the Rheinische Electricitätswerke. Although designed for a capacity of 200 tons per month, production ran as high as 250 tons monthly. The Horrem plant was closed in 1920 because of the power situation and because the Lautawerk had meanwhile come into production.

The third war-time plant was erected at Bitterfeld and secured current from the power plant of Chemische Fabrik Griesheim Elektron. The Bitterfeld works started operations in April, 1916, with an annual capacity of 3,000 tons and has operated continuously since that time.

Although these three works, designed for a production of 9,000 tons annually, were producing up to a rate of 12,000 tons per year, nevertheless, the supply of aluminum was quite inadequate, and additional works were designed and built with the cooperation of the government. Vereinigte Aluminium-Werke Aktiengesellschaft was formed on Apr. 21, 1917, with a capital of 50,000,000 marks. Half of the capital was subscribed by Griesheim Elektron and Metallbank, who brought into the new organization the plants at Rummelsburg, Horrem, and Bitterfeld. The Government supplied the other half and advanced additional large sums for the construction of the new plants. In addition to the reduction works, it was now necessary to build new plants

for the production of alumina, as well as a power plant for the electrical supply. In order to secure cheap fuel, the plants were located in the lignite district of Germany.

The first and largest of these plants was located in the district of Lausitz, near the town of Lauta, from which it took the name, "Lautawerk." A large tract of land, 1,200 acres in extent, was purchased and construction started in May, 1917. A steam power plant was erected which received its fuel from the nearby Erika mine of Ilse Bergbau, A.-G. Three turbines of 16,000-kilovolt-ampere capacity each and one of 18,000-kilovolt-ampere capacity furnished the necessary current, which, by means of rotary converters, was supplied to the reduction pots at 550 volts. Three pot rooms with a total capacity of 1,000 tons a month were constructed but only two were put into operation.

The plant for the production of alumina was designed with a capacity of 3,000 tons per month. Hungarian bauxite from the Bihar mountains was the chief source of ore. The bauxite was heated with soda ash in a rotary kiln; the product was ground, leached, filtered, and the alumina precipitated from the filtrate by agitating and cooling in the presence of a seed charge (Bayer method). The residual liquor was then carbonated to remove the remaining alumina and the soda ash was recovered for the next cycle.

The other plant, known as "Erftwerk," was located at Grevenbroich (Niederrhein) and was built by the government in cooperation with Giulini Brothers and Rheinische-Westfälisches Electricitätswerk. A carbon electrode plant was built in connection with Erftwerk. Steam power produced from lignite was used for generating current for both Lautawerk and Erftwerk.

In 1919, Griesheim Elektron and Metallbank retired from the Vereinigte Aluminium-Werke A.-G. and took over the operation of the Bitterfeld plant, which is operated under the company name of Aluminiumwerk G. m. b. H., Bitterfeld. The Erftwerk then came into the exclusive possession of Vereinigte Aluminium-Werke A.-G.

Innwerke Aktiengesellschaft was founded in 1917 by the Allgemeine Elektrizitäts-Gesellschaft, the Siemens Schuckertwerke, Giulini Brothers, the German Government, and the State of Bavaria. Power for this plant came from a hydro-

Fig. 10.—Location in Germany and Austria of aluminum reduction works (●) and alumina works (■).

Aluminum Reduction Works

{ Vereinigte Aluminium-Werke, A.-G.
Innwerk, Bayerische Aluminium, A.-G
Erftwerk, A.-G.
(Owned by Reichswerke, Berlin)
Aluminium-Werk, G.m.b.H.
(Owned by Metallgesellschaft, A.-G. and
I. G. Farbenindustrie, A.-G., Frankfort)
Aluminium Industrie, A.-G. (Neuhausen)
Aluminium Industrie, A.-G. (Neuhausen)
Aluminiumwerke Steeg
(Controlled by Stern und Hafferl)

1. Lautawerk, Lausitz, Germany
2. Innwerk, Töging, Oberbayern, Germany
3. Grevenbroich, Niederrhein, Germany

4. Bitterfeld, Germany

5. Rheinfelden, Baden, Germany
11. Lend-Gastein, Austria
12. Gmunden, Austria

Alumina Works

Vereinigte Aluminium-Werke, A.-G.
Tonerdewerke Curtius, G.m.b.H.
(Owned by Det Norske Nitridak-
tieselskab)

6. .   .   .   .   Germany
7.

electric development on the River Inn at Töging in Upper Bavaria; about 60,000 horsepower is available for the production of aluminum. Production was started in January, 1925. At the present time, the aluminum works belongs to Vereinigte Aluminiumwerke and the hydro-electric power plant is the property of Vereinigte Industrie-Unternehmungen A.-G. (VIAG) and the Bavarian State. Vereinigte Aluminium-Werke A.-G. now owns and operates three works, namely, Lautawerk, Erftwerk, and Innwerke. These three plants, together with the Bitterfeld works (without counting the small Rheinfelden works), give Germany a domestic production of about 30,000 tons annually. With the exception of Innwerke and the small Rheinfelden works, the German reduction works employ current generated by steam power. This condition is the result of lack of many large waterpower developments and the availability of cheap "brown coal" or lignite. It is quite in contrast, however, with the reduction works of all other countries, which employ hydro-electric power.

SWITZERLAND

Neuhausen, Switzerland, at the Rhine Falls, might well be called the "nursery" of the modern European aluminum industry.[1] J. G. Neher Sons, of Neuhausen, had been engaged in the iron and steel industry since 1810. Menaced more and more by foreign competition, they were seeking for a new industry which could use efficiently the waterpower available from the Falls of the Rhine. The manufacture of aluminum appeared to them to be an electrometallurgical process of considerable promise and one meeting their needs. In 1886, they experimented with the process of Kleiner, of Zurich, which involved the electrolysis of cryolite, but it was not found practicable.

It was in this same year, 1886, that Paul L. T. Héroult, a young French metallurgist, applied for patents on his process

[1] Bloch and Steck, of the Aluminium Industrie Aktiengesellschaft at Neuhausen, have kindly supplied many interesting details of the early history of the Neuhausen project, and it is largely upon their information that this account is based.

'onerdewerke Goldschmieden   8 Breslau, Germany
  (Owned by Aluminium Industrie, A.-G.)
'onerdewerk Martinswerk G.m.b.H.   9 Bergheim, Rheinland, Germany
'onerdewerk Gebr. Giulini G.m.b.H.   10. Ludwigshafen, Germany

of electrolyzing alumina dissolved in molten cryolite. He tried to interest various French manufacturers in his process, but without success. One of those approached was M. Péchiney, who was then engaged in making aluminum by the Deville chemical process at Salindres. Péchiney advised Héroult against attempting to manufacture pure aluminum and told him that there was more profit to be obtained in the manufacture of aluminum alloys, especially aluminum-bronze. Héroult then developed a process of making aluminum-bronze, for which he obtained an additional patent in 1887. This process, which has already been described, contemplated the electrolysis of fused alumina with a molten copper cathode and the absorption of the aluminum by the molten cathode to form aluminum-bronze. The electrolyte and copper cathode were maintained molten by the heat of the electrolyzing current.

In May, 1887, Héroult began negotiations with the representatives of J. G. Neher Sons and, on the twenty-sixth of August the same year, an agreement was reached to try out his alloy process at Neuhausen. The experiments were successful and, on the thirty-first of October, with the financial coöperation of other Swiss interests, the Schweizerische Metallurgische Gesellschaft was founded. The company took over Héroult's patent rights for all countries, with the exception of France; the French patents were held by M. Jules Dreyfus, of France.

With the personal assistance of Héroult, the production of aluminum-bronze and ferro-aluminum was rapidly commercialized. The first furnace, which was in operation during the summer and autumn of 1888, had a daily production of about 300 kilos of aluminum-bronze, with an average aluminum content of 20 per cent. At the end of 1888, operations were started with a larger furnace of the same type, which produced about 2,200 kilos of aluminum-bronze per day. At this time, there was concluded between the Schweizerische Metallurgische Gesellschaft and the Allgemeine Elektrizitäts-Gesellschaft, an agreement which resulted in the founding, on Nov. 12, 1888, of the Aluminium Industrie Aktiengesellschaft at Neuhausen.

At the same time, Dr. Martin Kiliani, who had been experimenting in the production of aluminum with the Allgemeine Elektrizitäts-Gesellschaft, was made managing director of the Aluminium Industrie Aktiengesellschaft. The works were enlarged in May, 1889, and the production of aluminum alloys

:ontinued on a larger scale. During the year 1889, experiments
vere made looking towards the production of pure aluminum,
ıs by this time The Pittsburgh Reduction Company's works
vere successfully operating by the Hall process in the United
5tates and demonstrating the advantages of the production of
)ure aluminum instead of the alloys.

There have been many conflicting statements made regarding
he contributions of Héroult and Kiliani to the development
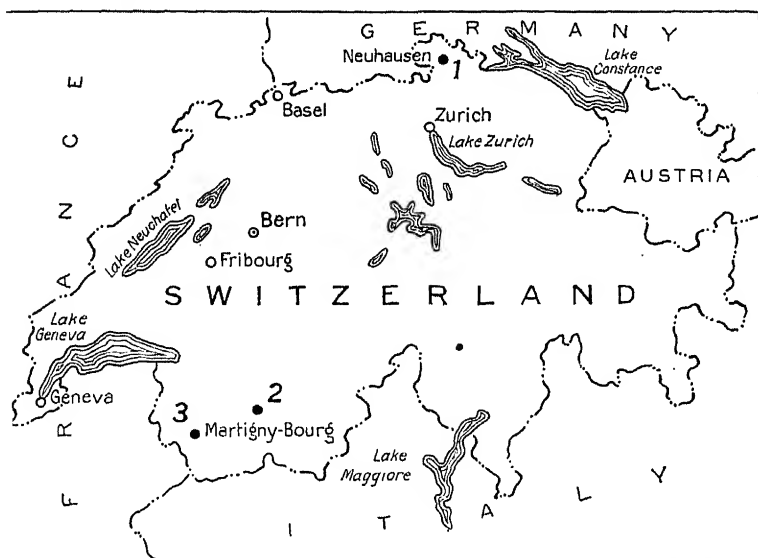)f the cryolite-alumina process at Neuhausen. Héroult applied

FIG. 11.— Location in Switzerland of aluminum reduction works (●).

Aluminum Reduction Works

luminium Industrie, A -G , or Societe   1. Neuhausen
Anonyme pour l'Industrie de l'Alumi-   2. Chippis
nium
ıbrique d'Aluminium Martigny, S. A.   3. Martigny-Bourg, Canton Valais

)r his patent covering this process and made pure aluminum
ıfore either he or Kiliani were connected with the Neuhausen
roject, and Héroult has explained that it was only on the advice
˙M. Péchiney that he undertook the production of aluminum
loys, rather than the production of pure aluminum. Kiliani
ıvented an electrolytic cell with a rotating anode,[1] but it did
ıt prove to be a success. Héroult and Kiliani found, however,
ıat the cells used in the production of the alloy could be adapted

[1] KILIANI, M., Ger. Pat. 50,508.

to the production of pure aluminum and they were so used.
Undoubtedly, considerable credit should be given to Kiliani for
his work in the commercial development of Héroult's process.

The management of the Aluminium Industrie Aktiengesell-
schaft has been in Swiss hands from its inception. Colonel
Huber-Werdmüller, who was chairman of the Schweizerische
Metallurgische Gesellschaft, became chairman of the new
company, and continued in that position until his death in 1915.
He was succeeded by Dr. Gustav Naville, who occupies this
position at the present time. The management was first in
the hands of Dr. Kiliani and Martin Schindler, but after the
death of Kiliani on Jan. 21, 1895, was in the hands of Schindler
until he retired in 1920. Much credit is due Naville and
Schindler for their energy and foresight in bringing the company
to its present position.

As in the case of the American Company, the Neuhausen
Company had considerable difficulty in finding a market for
aluminum, but, during the years 1890 to 1900, the industry
began to develop and their production facilities were expanded.
In 1897, a second works was started at Rheinfelden, Germany,
and late in the same year a third works was started at Lend-
Gastein, Austria. The most important works of this company
were begun in 1905 in the neighborhood of Chippis, Canton
Valais. Here there has been combined a system of five water-
power plants, which include one on the Navizance, near Chippis,
which was completed in 1908; one on the Rhone, near Chippis,
which was completed in 1911; one on the Borgne, near Bramois,
completed in 1913; and two, the Illseewerk and Turtmanwerk,
which were being completed in 1927 and 1928.

There is another aluminum reduction works in Switzerland
at Martigny-Bourg, Canton Valais. These works are owned
by Fabrique d'Aluminium Martigny, S. A.; their production
is about 1,800 tons per year.

NORWAY

Norway has a wealth of cheap electric power which is so
essential for the production of aluminum. Furthermore, many
of its waterpower developments are located on the coast and
provided with excellent harbors. The British Aluminium
Company was the first to recognize and take advantage of these
facilities. A Norwegian company, Aktieselskapet Stangfjordens

Elektrokemiske Fabriker, owned a partly developed waterpower site which was purchased in 1906 by the British Aluminium Company. They proceeded to erect aluminum works at Stangfjord, which is located on the west coast of Norway, about 100 miles north of Bergen. Production of aluminum was commenced there in January, 1908.

In April, 1907, a company known as the "Anglo-Norwegian Aluminium Company, Ltd.," was formed for the purpose of producing aluminum at Vigelands, near Kristianssand, South Norway. The Norwegian operating company was known as 'Aktieselskapet Vigelands Brug." The Anglo-Norwegian Aluminium Company did not prosper and in July, 1912, the British Aluminium Company purchased A/S Vigelands Brug and have continued the production of aluminum to date.

Another large Norwegian producer is known as "Det Norske Nitridaktieselskab," sometimes referred to as "D. N. N." This company was formed Aug. 20, 1912, by the Société Générale les Nitrures in coöperation with Det Norske Aktieselskab for Elektrokemisk Industri. The original intention was to manufacture alumina and nitrogen compounds by means of the Serpek process. This process, however, did not work out successfully and in 1913 they began to consider the production of aluminum. Their first works were erected at Eydehavn, which is near Arendal on the Kristianiafjord. Production was started here in 1914. The works had at its disposal about 25,000 horsepower furnished by the Boejlefoss power plant belonging to Arendals Fossekampani. The capacity of this works was doubled in 1916, when its production was brought up to about 5,000 tons per year. Electrodes for both Eydehavn and Tyssedal are made here.

Det Norske Nitrid has another works at Tyssedal, which commenced production in 1916. It is located on the Soerfjord, at the end of the Hardanger fjord, north of Odda and at the mouth of the Tysse river. Its initial production was about 5,000 tons per year, but in 1925 it was enlarged to a capacity of 10,000 tons per year. Det Norske Nitrid is jointly owned by the British Aluminium Company, Compagnie A. F. C., and Aluminium Limited.

Another large Norwegian producer is known as "Norsk Aluminium Company," with works at Høyanger, Sognefjord with a production of about 6,500 tons. Construction of this works
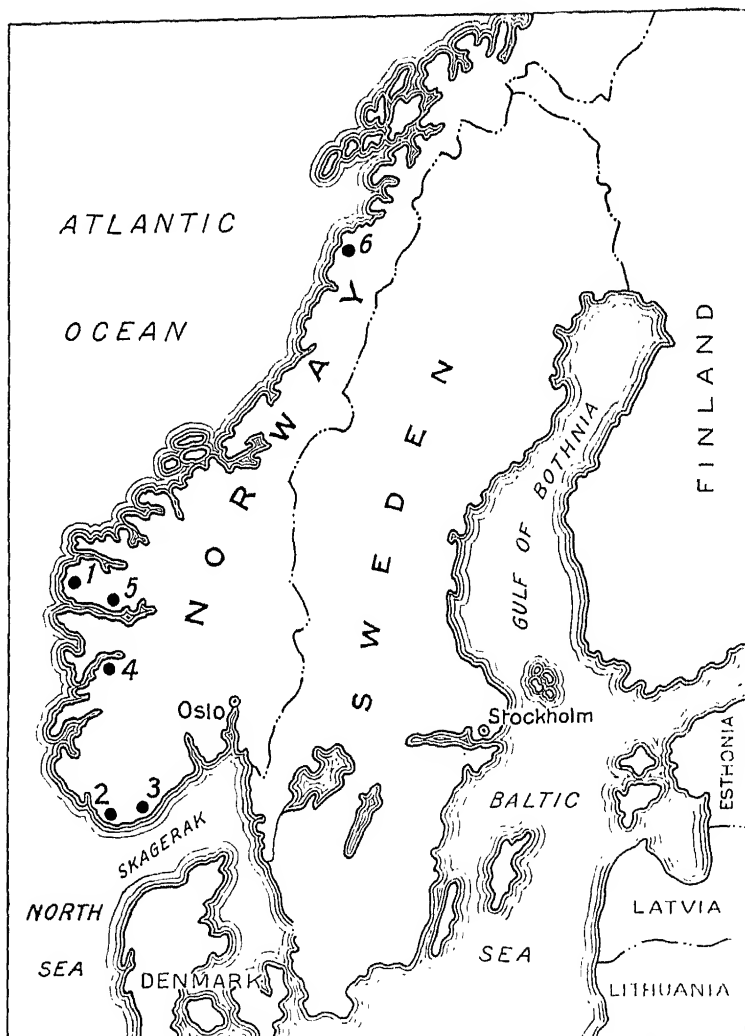
Fig. 12.—Location in Norway of aluminum reduction works (●).

Aluminum Reduction Works

Aktieselskapet Stangfjordens Elektrokemiske Fabriker	1. Stangfjord
(Owned by British Aluminium Company)	
Aktieselskapet Vigelands Brug	2. Vigelands
(Owned by British Aluminium Company)	
Det Norske Nitridaktieselskab	3 Eydehavn
(Owned by Compagnie A. F. C., British Aluminium Company and Aluminium Limited)	4. Tyssedal
Norsk Aluminium Company	5 Höyanger
(Jointly owned by Norwegian interests and Aluminium Limited)	
A/S Haugvik Smelteverk	6. Glomfjord

vas started in 1916. This concern was originally financed by
Norwegian capital, but after the World War, Aluminum Com-
pany of America acquired an interest which is now owned by
Aluminium Limited.

Aktieselskapet Haugvik Smelteverk, which is controlled by the
Aluminium Corporation, Limited, has been constructing works
at Glomfjord.

ITALY

Italy took no part in the early history of the aluminum
industry and up to the beginning of the twentieth century
imported its requirements of aluminum. In 1905, a supply
of bauxite became available from the opening of the mines at
Lecce de Marsi in the province of Aquila.[1] The first aluminum
reduction works were erected at Bussi (Aquila) on the Pescara
river in 1907. The bauxite supply came from the nearby Lecce
le Marsi mines. The Bussi plant is now controlled by the
Società Anonima Veneta dell' Alluminio (S. A. V. A.) and has an
annual capacity of about 1,000 tons. Alumina is produced
at works at Bussi di Tirene, (Aquila).

The Società dell' Alluminio Italiano, owned by Aluminium
Limited, is another Italian producer of aluminum. Its works
are located at Borgofranco d' Ivrea on the Dora Baltea and
have a capacity of about 1,400 tons per year.

During the war, the need for aluminum was greatly increased
and it was partly supplied by the Società Idroelettrica di Ville-
nueve from its plant at Nera Montuoro (Umbria). This plant
was constructed for the manufacture of chlorates and the
production of aluminum was discontinued after the armistice.

Aluminum is being produced by the Società Anonima Veneta
dell' Alluminio at its works at Porto Marghera, near Venice;
the annual production was about 1,000 tons in 1928. Alumina
is also produced in Italy by the Società Italiana dell' Alluminio
(Milan) with works at Mori.

Italy is the possessor of extensive deposits of a silicate of
potassium and aluminum known as "leucite." Efforts have
been made to recover both alumina and potash from leucite.
Perhaps the best known process is that of Baron Blanc, which
has been tried out on a semi-commercial scale.

[1] *Ind. Eng. Chem.*, News Ed., 12, Sept. 10, 1927.

Fig. 13.—Location in Italy and Jugo-Slavia of aluminum reduction works
(●) and alumina works (■).

Aluminum Reduction Works

Società dell' Alluminio Italiano
  (Owned by Aluminium Limited)
Società Anonima Veneta dell' Al-
  luminio (S.A.V.A.)
Società Italiana dell' Alluminio
  (Milan), (Owned by Montecatini)

1. Borgofranco d'Ivrea, on the Dora
  Baltea, Italy
2. Bussi (Aquila), on the Pescara, Italy
3. Porto Marghera, near Venice, Italy
4. Mori, Italy

Alumina Works

Società Anonima Veneta dell' Al-
  luminio (S.A.V.A.)
Chemische Fabrik (Formerly known
  as Giulini, G m.b.H., Laibach)

5. Bussi di Tirino, Aquila, Italy

6. Moste, near Ljubljana, Jugo-Slavia

pain.

Spain is the latest country to enter the aluminum producing
eld. Its only works are located at Sabiñanigo, Province of
[uesca, and are operated by Aluminio Español, S. A. Produc-
on started in October, 1927, and it is anticipated that the
nnual capacity will be about 1,200 tons a year.

ustria.

There are two aluminum reduction works in Austria. The
orks at Lend-Gastein, which are owned by Aluminium Indus-
ie, Neuhausen, have already been referred to. The second
orks are at Gmunden, Oberösterreich, and are known as
Aluminiumwerke Steeg." They are controlled by Elektrizi-
ätswerke Stern und Hafferl A.-G., and utilize, for the production
f aluminum, the surplus power left after supplying the public
tility requirements of the Stern und Hafferl group.

CHAPTER IV

ORES OF ALUMINUM

By

E. C. HARDER

Aluminum is the most abundant metallic element, forming, according to Clarke and Washington,[1] 8.05 per cent of the solid portion of the earth's crust to a depth of 10 miles. This is equivalent to an oxide content of 15.2 per cent Al_2O_3. The only more abundant elements in the earth's crust are oxygen (46.68 per cent) and silicon (27.60 per cent). Next to aluminum in abundance is iron (5.03 per cent), followed by calcium (3.63 per cent), sodium and potassium (2.72 and 2.56 per cent), and magnesium (2.07 per cent). The aluminum content of the earth appears to be concentrated near the surface; Washington[2] estimates the earth as a whole to contain only 1.79 per cent aluminum.

Aluminum is an important constituent in practically all common rocks except sandstone and limestone, and, even in these, it is nearly always present as an impurity. It is particularly abundant in such rocks as clay, shale, slate, argillaceous schist, granite, syenite, and anorthosite. Aluminum occurs in these rocks principally in the form of silicates of which the most abundant are the feldspars, micas, and various forms of clay. It also occurs relatively abundantly as oxides, chiefly hydrated, and the commercial ores of aluminum belong in this class. Table 1 shows the average range in the content of aluminum, calculated as Al_2O_3, in some of the more common rocks.

[1] CLARKE, F. W. and H. S. WASHINGTON, *Proc. Nat. Acad. Sci.*, **8**, 108 (1922).

[2] WASHINGTON, H. S., *Am. J. Sci.*, **9**, 351 (1925).

TABLE 1.—ALUMINUM CONTENT OF COMMON ROCKS

Kind of rock	Aluminum content calculated as Al_2O_3, percentage
Rhyolite and granite	11 to 16
Phonolite, trachyte and syenite	16 to 23
Andesite, diorite and monzonite	14 to 18
Basalt, gabbro and norite	12 to 21
Labradorite and anorthosite	26 to 32
Pyroxenite and peridotite	2 to 9
Average igneous rock	15.34[*]
Average shale	15.40[†]
Average sandstone	4.77[†]
Average limestone	0.81[†]

[*] CLARKE, F. W., H. S. WASHINGTON, *Proc. Nat. Acad., Sci,* **8,** 108 (1922).
[†] CLARKE, F. W., "The Data of Geochemistry," *U. S. Geol. Survey, Bull.* 695, 35 (1920).

Aluminum-bearing Minerals.

The principal minerals with moderately high aluminum content,[1] given roughly in the order of their abundance in the earth's crust, are as follows:

TABLE 2.—PRINCIPAL ALUMINUM-CONTAINING MINERALS

Name of mineral	Aluminum content calculated as Al_2O_3, percentage
Feldspars:	
Orthoclase, $K_2O.Al_2O_3.6SiO_2$	18.4
Albite, $Na_2O.Al_2O_3.6SiO_2$	19.5
Anorthite, $CaO.Al_2O_3.2SiO_2$	36.7
Micas:	
Muscovite, $K_2O.3Al_2O_3.6SiO_2.2H_2O$	28.5
Biotite, variable composition	15.0 $\pm$
Phlogopite, variable composition	15.0 $\pm$
Clay Minerals:	
Kaolinite (kaolin), $Al_2O_3.2SiO_2.2H_2O$	39.5
Halloysite, $Al_2O_3.2SiO_2.2H_2O$ aq	36.9
Allophanite (allophane), $Al_2O_3.SiO_2.5H_2O$	40.5
Leucite, $K_2O.Al_2O_3.4SiO_2$	23.5
Nephelite (nepheline), $3Na_2O.K_2O.4Al_2O_3.9SiO_2$	33.2
Analcite, $Na_2O.Al_2O_3.4SiO_2.2H_2O$	23.2
Scapolite, calcium-sodium-aluminum silicate	30.0 $\dagger$
Spodumene, $Li_2O.Al_2O_3.4SiO_2$	27.4
Pyrophyllite, $Al_2O_3.4SiO_2.H_2O$	28.3
Cyanite (kyanite), $Al_2O_3.SiO_2$	63.2

[1] DANA, E. S., "Textbook of Mineralogy," John Wiley & Sons, Inc.

TABLE 2.—PRINCIPAL ALUMINUM-CONTAINING MINERALS.—(*Continued*)

Name of mineral	Aluminum content calculated as Al_2O_3, percentage
Sillimanite, $Al_2O_3.SiO_2$	63.2
Andalusite, $Al_2O_3.SiO_2$	63.2
Dumortierite, possibly $4Al_2O_3.3SiO_2$	variable
Staurolite, $2FeO.5Al_2O_3.4SiO_2.H_2O$	55.9
Gibbsite (hydrargillite), $Al_2O_3.3H_2O$	65.4
Diaspore, $Al_2O_3.H_2O$	85.0
Corundum, Al_2O_3	100.0
Alunite, $K_2O.3Al_2O_3.4SO_3.6H_2O$	37.0
Alunogen, $Al_2(SO_4)_3.18H_2O$	variable
Pickeringite, $Al_2(SO_4)_3.MgO.SO_4.22H_2O$	variable
Spinel, $MgO.Al_2O_3$	71.8
Hercynite, $FeO.Al_2O_3$	58.6
Gahnite, $ZnO.Al_2O_3$	55.7
Wavellite, $4AlPO_4.2Al(OH)_3.9H_2O$	38.0
Cryolite (kryolith), $3NaF.AlF_3$	24.3

Of the above minerals, the feldspars are by far the most abundant because they are the principal constituents of igneous rocks. Moreover, undecomposed feldspars are always present in such sedimentary rocks as shale, arkose, and graywacke. The micas are similar to the feldspars in their occurrence and distribution and are especially abundant in metamorphosed sediments and igneous rocks. The clay-forming minerals, such as kaolinite, halloysite, allophanite, and others, result mainly from the decomposition of feldspars and other aluminum silicates; they and the micas are, therefore, very abundant in decomposed igneous rocks and in various sedimentary and metamorphic rocks, such as clay, shale and slate. The feldspathoid minerals, leucite, nephelite and analcite, are constituents of certain types of syenitic rocks locally abundant. Scapolite and spodumene occur mainly in igneous rocks. Pyrophyllite is an aluminum silicate resembling the magnesium silicate, talc; like the latter, it is found in metamorphic schists or metamorphosed volcanics. Sillimanite, andalusite, cyanite and staurolite are found in metamorphosed sedimentary rocks, particularly in slates and in various argillaceous schists. The hydrated aluminum oxides, gibbsite (or hydrargillite) and diaspore are locally associated with certain sedimentary rocks, principally clays and limestones, but they also occur abundantly as decomposition products of igneous rocks. Corundum occurs in igneous and metamorphic rocks, being

rmed either as an original constituent or by recrystallization
 other aluminous materials, as a result of heat or pressure.
unite occurs as an alteration product of rocks, generally result-
g from volcanic action. Alunogen and pickeringite are chemical
ecipitates often occurring as efflorescences or in playas in desert
gions. The minerals of the spinel group are products of con-
ct and regional metamorphism and also occur in volcanic rocks.
avellite and cryolite are of local occurrence only.

Besides the above minerals there are others such as the
mphiboles, pyroxenes, and garnets, the aluminum content of
hich, although relatively small in each individual, is large in
e aggregate as they are important constituents of many
eous and metamorphic rocks.

The literature of aluminum ores and minerals contains a
mber of other terms such as bauxite, laterite, terra rossa,
homarge, bauxitic clay, and diasporic clay. Most mineralo-
sts agree, however, that these terms have no definite chemical
 mineralogical significance and that each may be applied to a
nsiderable variety of materials.

ALUMINUM ORES AND RELATED MATERIALS

auxite.

Bauxite, although not named so until many years later, was
scovered by the French chemist, P. Berthier, when in 1821 he
vestigated specimens of this material found near Les Baux
 southern France. The substance examined by Berthier
as an aluminous, ferruginous rock of the following composition:
l$_2$O$_3$, 52 per cent; Fe$_2$O$_3$, 27.6 per cent; H$_2$O, 20.4 per cent;
r$_2$O$_3$ trace, in which the aluminum oxide was supposed to be
esent in the form of the dihydrate, Al$_2$O$_3$.2H$_2$O. For many
ars the term "bauxite" was used mineralogically to designate
e dihydrate of aluminum,[1] and, even at the present time, some
vestigators believe in the existence of such a dihydrate and
ll it "bauxite."[2] The term also came to be widely used in a
neral sense to cover the various kinds of aluminum ores,
nsisting mainly of hydrated aluminum oxides, which were
scovered in various parts of the world. These ores, besides
ffering in the amounts and kinds of impurities, were found,

[1] DANA, E. S., *loc. cit.*

[2] RAO, T. V. M., "A Study of Bauxite," *Mineralog. Mag.*, **21**, No. 120,
7–430, March, 1928.

upon analysis, to vary in their content of chemically combined water and this, together with the fact that a definite crystalline dihydrate of aluminum oxide has not been isolated, led most investigators to conclude that probably the dihydrate does not exist as a definite mineral; whereas, on the other hand, the monohydrate (diaspore and α-monohydrate) and trihydrate (gibbsite) do exist as definite minerals. This conclusion is strengthened by certain phenomena shown by the heating curves of many aluminum ores. When gibbsite and diaspore are heated in order to drive off the chemically combined water, definite arrest points appear on the heating curves, these arrest points differing in the two minerals. Many aluminum ores, when similarly heated, show the arrest points of both gibbsite and diaspore but no arrest point for any other possible aluminum hydrate. A smooth curve connects the arrest points, probably indicating the presence of aluminum hydrates in the gel form that evolve water at a considerable range of temperature.[1]

At present, the term "bauxite" is, therefore, applied to aluminum ores generally believed to consist of a mixture, in different proportions, of the trihydrate and the monohydrate, with certain impurities. The impurities are principally the ferric oxide, hematite, various hydrated ferric oxides, such as goethite and xanthosiderite,[2] and silica, usually present, combined as kaolinite and halloysite, but sometimes free, as quartz. Besides these, there is always titanium present, possibly in the form of an unnamed hydroxide, possibly as rutile, ilmenite, or leucoxene,[3] or possibly in the form of the hydrous aluminum titanate, xanthitane.[4] Locally, in minor quantities, occur magnetite, ferrous carbonate (siderite), calcium and magnesium carbonates, iron sulphide, aluminum phosphate (probably wavellite), or manganese oxides. Bauxite may, therefore, be defined as an aluminum ore, more or less impure, in which the aluminum is largely present as hydrated oxides.

Much bauxite is amorphous or is so finely crystalline that individual minerals are indistinguishable. Many investigators,

[1] KNIBBS, N. V. S., "The Industrial Uses of Bauxite," pp. 46–49, Ernest Benn Ltd., London (1928).

[2] CAMPBELL, J. M., "The Origin of Laterite," *Trans. Inst. Mining Metallurgy*, **19**, 432–443 (1909–1910).

[3] COGHILL, W. H., "Titanium in Bauxite Ores and Sludges," *U. S. Bur. Mines, Repts. Investig., Ser.* 2,867, April, 1928.

[4] CLARK, F. W., *loc. cit.*, p. 495.

refore, claim that the aluminous, ferruginous, and siliceous
mponents are present in such cases not as definite minerals but
colloidal form as uncombined oxides or hydrogels. Some[1]
sider as possible the presence in bauxite of more or less definite
orphous hydrated aluminum oxides, the colloidal equiva-
ts of gibbsite and the monohydrate. Similarly, it is sug-
ted that definite colloidal hydrated oxides of iron may be
sent, such as stilpnosiderite, the colloidal equivalent of limo-
, and others.

The bauxites of any given district generally have certain
mon characteristics as to composition and impurities. Thus
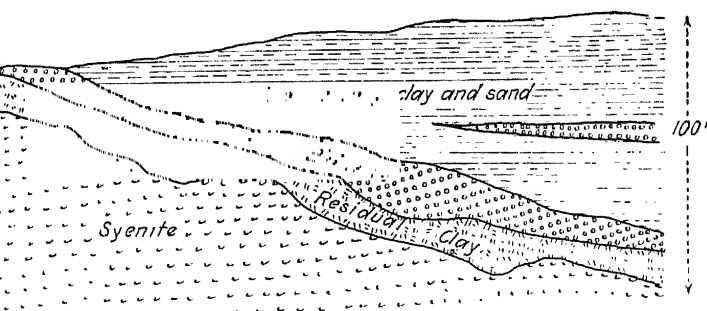
Fig. 14.—Section of typical bauxite deposit in Arkansas.

bauxites of southern France in most places carry 57 to 60
cent alumina, 20 to 25 per cent ferric oxide, 3 to 5 per cent
ca, and 11 to 13 per cent combined water; those of Dalmatia
also high in ferric oxide and low in silica (1 to 3 per cent),
, contain about 48 to 55 per cent alumina and 20 to 22 per
t combined water; those in the United States range from 56
59 per cent in alumina, 27 to 30 per cent in combined water,
l contain from 5 to 12 per cent silica, but are low in ferric oxide,
many places containing 1 to 3 per cent and only locally con-
ing more than 5 or 6 per cent, while those of the Guianas
erally contain 56 to 61 per cent alumina, 29 to 31 per cent
bined water, 1 to 3 per cent silica, and a variable amount of
ric oxide. In certain districts, minor constituents play
ortant roles. Thus, certain bauxites of India contain 8 to
per cent or more titanium oxide instead of the usual 2.5 to
er cent. Some deposits in Istria, Montenegro, and in the

LACROIX, A., "Les Laterites de la Guinée et les Produits d'Alteration,"
w. Arch. du Mus., **5**, Paris (1913).

United States have a bluish color in parts due to the presence of ferrous sulphide or ferrous sulphate. Some Russian bauxite deposits are characterized by their high calcium-carbonate content and the abundance of free quartz. The bauxite of Mississippi is locally rich in siderite. Certain deposits on the northern coast of Brazil are rich in aluminum phosphate, ranging from 15 to 25 per cent in P_2O_5.

Not only the chemical composition but also the physical appearance of bauxite varies greatly. Some varieties have a pisolitic or oolitic texture; many are dense and fine grained with conchoidal or blocky fracture, others have a granitic texture and still others are porous or vesicular. Most bauxite is moderately hard and compact but soft earthy bauxite occurs. There are also gradational phases between the bauxites of different textures. Bauxite pisolites may be dense and solid, often with concentric spheres, or they may have soft or hollow interiors.

Dana[1] gives the specific gravity of bauxite as 2.55, that of gibbsite as 2.3 to 2.4, and that of diaspore as 3.3 to 3.5. On the above basis 14 cubic feet of bauxite would weigh 1 gross ton. In practice, however, it has been found that on account of the porous texture it is conservative, for purposes of estimating tonnages, to use 23 cubic feet as the volume of 1 gross ton of ordinary low iron bauxite, and 19 cubic feet as the volume of 1 gross ton of dense high iron bauxite.

As regards color, bauxite when low in iron oxide is usually white, gray, or cream colored; when containing a moderate amount of ferric oxide it may be pink, yellow, light brown, or light red, and when high in iron oxide it is dark red or brown. The coloring is independent of the texture. Moreover, dark red pisolites may be found in a gray or pink groundmass, or fine grained or vesicular bauxite may show yellow, brown, and dark-red mottling. All combinations occur.

Laterite.

Laterite is a term that pervades the more recent literature on aluminum ores and is found in much of the older literature. It was first applied in 1807, by Francis Buchanan, to a more or less consolidated residual rock formed by surface weathering in the Malabar and Kanara territories of southern India. In 1883, F. R. Mallet[2] noted the high-alumina content of certain

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[1] DANA, E. S., *loc. cit.*, pp. 348, 350, 351.

[2] MALLET, F. R., *Records Geol. Survey India*, **16**, 103 (1883).

terities in the Katni region in the central part of India. The composition of the rock found by Buchanan is not known.

Since the discovery and naming of the original laterite of India, similar rocks formed under approximately the same conditions have been found in many different countries, especially in various parts of tropical Africa, South America, the East Indies, and Australia. In these tropical countries, the laterite occurs in the form of flat-lying surface blanket deposits, in places many miles in extent and varying in thickness from a few inches to 75 feet or even more. (See Figs. 18 and 19.)
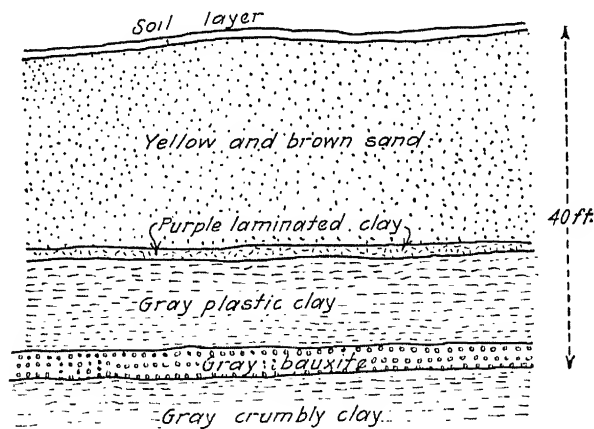
Fig. 15.—Section of typical bauxite bed in coastal plain region, Georgia.

Moreover, laterite deposits formed in past geologic periods and now occurring as layers and lenses interlayered with other sedimentary rocks or along contacts between igneous and sedimentary rocks have been found in countries which now have temperate climates but in which, at the time the laterite was formed, tropical or subtropical conditions probably prevailed.

The type of tropical or subtropical surface alteration which results in the formation of laterite is called "lateritization" (or laterisation). It results in concentrating, in the surface layer, the less soluble rock constituents, such as the oxides or hydrated oxides of iron, aluminum, titanium, and manganese, together with variable quantities of clay and quartz. The proportions of these constituents vary widely, depending on the composition of the original rocks and on the degree of lateritization. Some laterites, as those in British and Dutch Guiana,

West Africa and central India, consist mainly of bauxite and these may be high-grade aluminum ore. Some, as those in northeastern Cuba, consist mainly of iron oxides and may be rich enough to be commercial iron ore; others, as those in southern India, may contain important percentages of manganese oxide, and still others may consist mainly of high-iron or high-alumina clay or lithomarge.

Attempts have been made to limit the application of the term "laterite" and to give to it a definite petrological or chemical significance, emphasizing its percentage of hydrated aluminum and iron oxides.[1] Since, however, we know neither the mineralogical nor the chemical composition of the rock to which Buchanan first applied the term "laterite," and considering that this term has been applied subsequently to materials of widely varying composition, such a restriction does not seem warranted.   It seems more reasonable to use the terms "bauxite" and "iron ore" when petrological or chemical qualities are under discussion and "laterite" when general geologic relations are being considered.   A laterite formation really consists of a number of separate petrologic units, either interlayered, intermixed, or irregularly distributed from place to place, in the same manner as a shale formation may consist in one place of typical clay shale and elsewhere of limey shale, siliceous shale, shaley limestone, or shaley sandstone.   The term "laterite," therefore, while in part a duplication of the term "bauxite," has a wider application and is more inclusive.   Moreover, usage has given it a stratigraphical or genetical rather than a petrological significance.

Fermor[2] in discussing the character and manner of occurrence of laterites divides them into two main groups, (*a*) chemically formed laterites and (*b*) detrital laterites or lateritites.   The chemically formed laterites he subdivides into three classes: (1) true laterites, formed by weathering in situ; (2) lake laterites, formed by chemical deposition in lakes or other bodies of water, and (3) lateritoids, formed by metasomatic replacement of rocks.   These terms are somewhat misleading as they give the impression that different kinds of laterite are formed by separate and distinct processes, whereas, in fact, most laterites are formed

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[1] FERMOR, L. L., "What is Laterite?" *Geol. Mag.*, Decade V, **8**, October, November, December, 1911.

[2] FERMOR, L. L., *loc. cit.*

by a combination of processes, including decomposition, replacement, and recrystallization.

Terra Rossa.

The term "terra rossa" (red earth) has been widely applied to a dark-red loose soil derived from the weathering of limestone. It is commonly associated with bauxite deposits in limestone areas. In the bauxite districts of Istria, Dalmatia, and southern France, terra rossa occurs as a blanket over the deposits and surrounding limestone, as an irregular layer between the bauxite and the enclosing limestone, or irregularly intermixed with the bauxite. Although ordinarily used in connection with products of limestone decay, the term "terra rossa" need not necessarily be restricted to this use. Red earths similar in appearance and composition to those overlying limestone in southern Europe and elsewhere are common in many tropical regions, being derived from the decomposition of various kinds of igneous rocks, and being frequently associated with laterite. Terra rossa is an aluminous, ferruginous clay or soil containing, in appreciable quantity, oxides or hydrated oxides of aluminum and iron, as well as silica in the form of quartz, chalcedony, or as silicates. In the case of terra rossa derived from limestone in Croatia, Kispatic[1] believes that the hydrated aluminum oxide was originally present in the limestone as such, rather than having been derived by weathering from aluminum silicates in the limestone. Kerner von Marilaun,[2] however, believes that some aluminum hydrate is certainly derived from silicates. Moreover, in tropical regions red earth is undoubtedly formed from the decomposition of iron and aluminum silicates.

Lithomarge.

The term "lithomarge" is used by Dana[3] to designate an impure compact form of kaolin, or, in other words, a hard, compact clay. In certain publications by members of the Geological Survey of India treating with laterites, a hard, compact material approximating the composition of kaolinite

[1] KISPATIC, M., "Bauxite des kroatischen Karstes und ihre Entstehung," *Neues Jahrb.*, **34**, 513 (1912).

[2] KERNER VON MARILAUN, F., "Geologie der Bauxitlagerstäten des südlichen Teiles der Österreichisch-Ungarischen Monarchie." *Berg- und Hüttenmänn Jahrb.*, pp. 139-170 (1916).

[3] DANA, E. S., "Textbook of Mineralogy," p. 481.

but of amorphous texture is termed "lithomarge." This definition, and the physical properties of much of the Indian lithomarge, apply more nearly to halloysite, a common associate of bauxite and, in many places, a constituent in laterites. Fermor[1] proposes to apply the term "lithomarge" to the constituents in laterite containing combined silica and such usage would for the most part include impure kaolinite, impure halloysite, mica, and other clay-forming minerals. Thus, there is no precise agreement as to the definition of the term "lithomarge." If Dana's definition were extended to include, besides impure kaolinite,
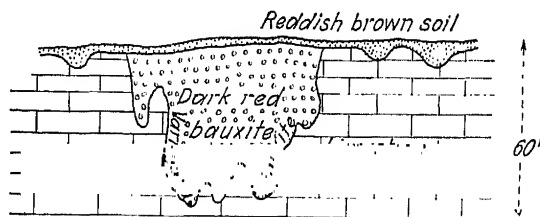
FIG. 16.—Section of typical bauxite pocket in Istria.

impure forms of non-crystalline hydrous aluminum silicates, such as halloysite and allophanite, this usage would be general enough to cover most conditions, and in this sense the term would have a useful meaning.

Bauxitic Clay.

Bauxitic clay is a term widely used to designate a clay in which the percentage of alumina is greater than in kaolinite or halloysite. It seems probable that this excess of alumina is present in the form of hydrated aluminum oxides.[2] Bauxitic clay may be soft, mealy and friable or plastic, or moderately hard and compact. In many places it is pisolitic. It is commonly associated with bauxite; in many places it underlies or borders bauxite deposits. In addition to silica it generally contains about the same other impurities as the bauxite but in less amount, the titanium oxide and iron oxide contents being usually lower than in the associated bauxite. The alumina content of bauxitic clays ranges from 40 to 50 per cent or more.

[1] FERMOR, L. L., "What is Laterite?" *Geol. Mag.*, Decade V, **8**, October, November, December, 1911.

[2] EDWARDS, M. G., "The Occurrence of Aluminum Hydrates in Clays," *Econ. Geol.*, **9**, 112–121 (1914).

iasporic Clay.

Certain flint fireclay deposits in east central Missouri[1] and entral Pennsylvania have associated with them, in irregular nasses of varying size, hard, rough-textured clay, with irregular acture and a high alumina content caused by the presence of olites and pisolites of diaspore. This clay is known as "burley lay" when moderately high in alumina and as "diasporic clay" hen very high in alumina. Masses of impure diaspore locally ccompany this clay. Burley clay and diasporic clay range in lumina content from 50 to 75 per cent. They might properly e included under the broader term "bauxitic clay," but they iffer from ordinary bauxitic clays in their hardness, their rough neven texture, and their association with diaspore.

USES OF ALUMINUM-BEARING MINERALS AND ORES

The most important use of aluminous minerals and rocks is in he ceramic industries for the manufacture of bricks, tiles, uilding blocks, earthenware, pottery, china, porcelain, and nany other articles. For this purpose the use of bauxite is rare; lay, shale, kaolin, and other aluminum silicate-bearing materials eing commonly used. China requires special high-grade kaolin nd clay. Feldspar is widely used in porcelain manufacture. yanite, andalusite, and sillimanite are used to make spark plugs. ure alumina (Al_2O_3) prepared from bauxite is used in the nanufacture of certain varieties of glass.

Next in importance is the use of aluminum ores for the pro-luction of alumina for the aluminum industry. Aluminum was irst made experimentally from cryolite but later alumina (Al_2O_3), xtracted from bauxite, was used in its manufacture and, today, ractically all alumina for the aluminum industry is produced rom bauxite. Low-grade laterites and aluminum silicates, such s clays, have been used experimentally for the production of luminum but their use at present is commercially impracticable. for aluminum manufacture, bauxite should be rich in alumina nd as low as possible in impurities, particularly in silica and itanium oxide.

Aluminous refractory products, such as refractory bricks nd forms used for furnace linings, require large quantities

[1] McQUEEN, H. S. and C. R. FORBES, "The Geology and Mining of iaspore and Flint Fire Clays of Missouri," *Trans. Am. Inst. Mining Met. ng.*, New York meeting, February, 1928.

of aluminum-bearing materials in their manufacture. High alumina clays (bauxitic clay and diasporic clay) are used largely for this purpose but considerable quantities of bauxite or alumina prepared from bauxite are used. Recently cyanite, sillimanite, and other aluminum silicates have also come into use for the manufacture of refractory products.

There are two main classes of aluminous refractories (*a*) those in which fused alumina or artificial corundum is the refractory constituent and (*b*) those to which mullite ($3Al_2O_3.2SiO_2$),
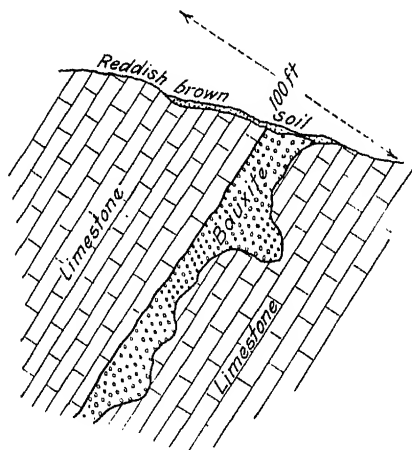
Fig. 17.—Section of typical bauxite bed in Dalmatia.

an artificial aluminum silicate, imparts the refractory qualities.[1] The first are manufactured from alumina or bauxite bonded with clay, while the second are prepared by fusing a mixture in the proper proportions of alumina or bauxite with silica, or by fusing cyanite, sillimanite, andalusite, or dumortierite. Even ordinary fireclay brick, however, after prolonged furnace action develops mullite crystals.

Large tonnages of bauxite are annually consumed in the manufacture of artificial aluminous abrasives. Among the important artificial aluminous abrasives manufactured in the United States and Canada are Alundum, Aloxite, Borolon, and Lionite. They are produced by the fusion of bauxite at high temperatures in electric furnaces. The fused material is then

[1] Bole, G. A., "Some Refractories now in Process of Development," *Eng. Mining J.*, **125**, 982–83, 1023, June 16, June 23, 1928.

inely crushed and either mixed with a bonding substance and molded into grinding wheels, whetstones, etc., or used as abrasive powder. Bauxite moderately low in silica and high in alumina s desirable for this use. Prepared alumina is used for the manufacture of special high-grade abrasive products.

The chemical industries also require large quantities of bauxite, particularly for the manufacture of aluminum sulphate and aluminum chloride. Aluminum sulphate, which is widely used in paper manufacture and for the purification of water, requires a bauxite low in iron oxide so that the resulting product may be as free from color as possible. When high-grade, iron-free aluminum sulphate is required, pure hydrated aluminum oxide $Al(OH)_3$), obtained by refining bauxite, is used. Various alums, such as potash alum, ammonia alum, and soda alum, are manufactured from aluminum sulphate. Aluminum chloride s used extensively as a catalyst for "cracking" purposes in petroleum refining to produce the maximum amount of gasoline and other light oils.

In recent years bauxite has been used in increasing quantities for the manufacture of special quick-hardening high-alumina cements. These cements are prepared in blast furnaces, rotary kilns, or electric furnaces by the fusion of bauxite and limestone, the resulting product consisting of a mixture of calcium aluminates and calcium-aluminum silicates with some iron oxide and probably some calcium silicates.

Some bauxite is used in oil filtration as a decolorizing and deodorizing agent. Apparently, bauxite ground to a size ranging from 30 to 60 mesh and heated to 400°C. is in certain respects more efficient than fuller's earth for the removal of unsaturated colored hydrocarbons and sulphur compounds from oil.[1] Regeneration of used material is possible by heating in rotary kilns.

Dark-red high iron bauxite is used locally for pigment manufacture.

GEOLOGY OF ALUMINUM ORES

Bauxite and laterite deposits have been described as occurring in a number of different geologic relations but in general all of them can be grouped into four main classes.

[1] KNIBBS, N. V. S., "The Industrial Uses of Bauxite," pp. 101–107, Ernest Benn, Ltd., London (1928).

1. Blanket deposits occurring at or near the surface in horizontal or nearly horizontal sheets and lenses. (See Figs. 18 and 19.)

2. Beds and lens-like deposits occurring at definite stratigraphic horizons interlayered with sediments or between sediments and igneous rocks. (See Figs. 14, 15 and 17.)

3. Pocket deposits or irregular masses enclosed within limestone or clay. (See Fig. 16.)

4. Detrital deposits formed by the mechanical breaking up, transportation, and redeposition of material from deposits of the other three types.

These four types of deposits are closely related to each other and are in many places gradational. There is a strong probability that the first three have originated in a somewhat similar manner.

<div align="center">TABLE 3.—AGE RELATIONS OF BAUXITE DEPOSITS</div>

Pleistocene and Recent	Tropical laterite deposits.
Cenozoic:	
Pliocene	
Miocene	German bauxite (Vogelsberg Mountains).
Oligocene	Irish bauxite (County Antrim).
Eocene:	
Upper	
Middle	
Lower	United States bauxite—underlain by Lower Eocene or Lower Cretaceous.
	Dalmatian bauxite—underlain by Lower Eocene and Upper Cretaceous.
	Montenegran bauxite (Bar and Ulcinj)—underlain by Upper Cretaceous.
	Istrian bauxite—underlain by Upper Cretaceous.
	Spanish bauxite—underlain by Eocene and Rhoetic.
	Kashmir deposits (Jammu) underlain by Jurassic.
	Hungarian bauxite—underlain by Rhoetic.
Mesozoic:	
Cretaceous:	
Upper,	
Danian	
Senonian	Greek bauxite—underlain by Jurassic.
	French bauxite (Herault)—underlain by Jurassic
Middle,	
Turonian	
Cenomanian	

TABLE 3.—AGE RELATIONS OF BAUXITE DEPOSITS.—(*Continued*)

Albian	French bauxite (Var)—underlain by Urgonian, Neocomian and locally Jurassic.
	Italian bauxite (Central Apennines).
	Montenegran bauxite (Kotor and Niksic)—underlain by Lower Cretaceous.
Lower,	
Aptian	
Urgonian	French bauxite (Ariège)—underlain by Jurassic.
Neocomian	Rumanian bauxite (Bihar)—underlain by Malm.
Jurassic:	
Malm	
Dogger	
Lias	
Triassic:	
Upper { Rhoetic	Croatian bauxite—underlain by Middle Triassic.
Middle { Keuper	
Lower	
Paleozoic:	
Upper Carboniferous	Missouri diaspore—underlain by Upper Carboniferous.
Lower Carboniferous	Russian bauxite (Tikhvin)—underlain by Devonian.
Devonian	

Blanket Deposits.

Horizontal blanket deposits are found usually in tropical or semitropical regions, where they occur on peneplained surfaces or as cappings on extensive plateaus (or flat-topped hills which are outliers of such plateaus), which represent peneplains that have been elevated and have suffered erosion subsequent to peneplanation. In many places the laterite or bauxite deposits are at the surface, which is then only sparsely covered with vegetation; in other places a varying thickness of soil covers the laterite. Generally, the surface and upper portions of the laterite or bauxite are hard and indurated, in most places as the result of infiltration and cementation by iron oxide. With depth, the laterite or bauxite becomes softer and at the base it is generally moderately soft and grades into the underlying clay or lithomarge. In places, irregular pencil-like projections extend downward from the base of the laterite into the clay, or else vesicular masses of bauxite, or a reticulated network of bauxite pencils impregnates the upper part of the underlying clay. (See Fig. 19.)

Laterite blanket deposits range in thickness from less than 1 foot to 75 feet or more. The average is from perhaps 5 to about 20 feet. Horizontally, the deposits may extend from a few hundred feet to several miles. The entire layer, except for variations at the immediate surface or at the base, may be fairly uniform and consist of high-grade bauxite, ferruginous or siliceous bauxite, bauxitic or ferruginous clay, or iron ore. On the other hand, there may be a variation both vertically and horizontally with the individual constituents lying in well-marked layers or being irregularly intermixed. The layering in laterite in some places, for example in India, is described as being quite regular and uniform over large areas.[1]

The age of surface deposits of bauxite may vary considerably in different districts. Many of the deposits are forming at the present day, these being mainly the low-level peneplain deposits. The plateau or high-level deposits were formed during long periods of peneplanation preceding their elevation and such elevation may have been fairly recent or may date back to Quaternary or even Tertiary time.

Among the more important localities in which bauxite and laterite deposits are found in the form of surface blankets are India, the East Indies, New South Wales, Victoria, Western Australia, Seychelles Islands, Madagascar, Mozambique, Nyasaland, Nigeria, Kamerun, Togoland, Gold Coast, French Guinea, Brazil (Minas Geraes and Maranhao) and the colonies of French, Dutch, and British Guiana.

Interlayered Deposits.

Most layers and lenses of bauxite or laterite interbedded with sediments or lying between sediments and igneous rocks are what might be termed "fossil deposits." They represent surface blanket deposits of past geologic ages that have been submerged subsequent to their formation and have had deposited upon them successive beds of later sediments.

As far as texture and composition are concerned, interbedded laterite deposits resemble the surface laterites closely, except that they have a tendency to be harder, more compact, and more indurated and have less combined water. They show the same variations in grade, however, and have the same impurities.

[1] Fox, C. S., "The Bauxite Resources of India," *Mineralog. Mag.*, pp. 82–96, February, 1922; also Fox, C. S., "Bauxite," Crosby Lockwood & Son, London (1927).

In many places the rocks in which the laterite and bauxite layers and lenses are embedded have suffered deformation, with resultant folding and faulting of the laterite or bauxite layers.

In age, the interbedded bauxite layers range from Paleozoic to Quaternary but apparently the most widespread and intensive lateritization periods occurred in the Middle Cretaceous and in the Lower Eocene.   (See Table 3.)

The oldest laterites, as far as our present knowledge goes, are those of the Tikhvin district in northwestern Russia which
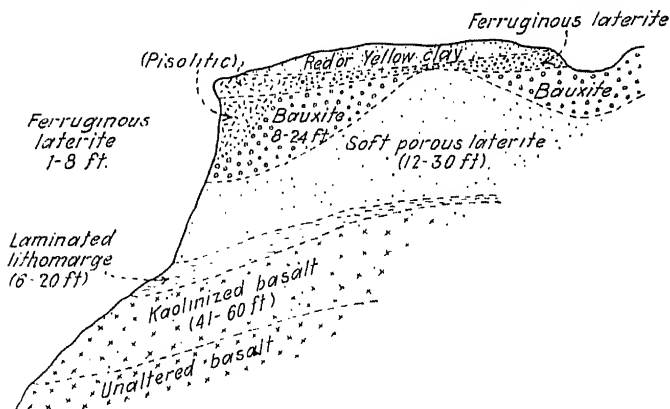
Fig. 18.—Section of part of typical laterite plateau (in India) with bauxite. (*After Fox.*)

were formed at the end of Devonian or at the beginning of Lower Carboniferous time.   These deposits consist of low-grade ferruginous and siliceous laterite with some bauxite, and occur as lenses along a definite stratigraphic horizon with Lower Carboniferous partly consolidated clay and sand overlying them and Devonian micaceous clay and sand underlying them.

Next in age are the diasporic clay occurrences of east central Missouri.   The diasporic clay is found as irregular masses in pockets of flint clay enclosed in the Cherokee Sandstone of Pennsylvanian (Upper Carboniferous) age.   The sandstone with included clay pockets is found in sinkhole-like depressions on the surface of the Jefferson City and Gasconade dolomites of Ordovician age.[1]   The flint clay pockets are numerous but

[1] McQueen, H. S. and C. R. Forbes, "The Geology and Mining of Diaspore and Flint Fire Clays of Missouri," *Trans. Am. Inst. Mining Met. Eng.*, New York meeting, February, 1928.

small, ranging from 75 to 100 feet in diameter and averaging about 50 feet in depth.

The oldest bauxite of Mesozoic age is that of the Velebit Mountain region in Croatia which is found in Upper Triassic rocks. It occurs as impure lenses in the Raibler limey, ferruginous sandstones which are overlain by Hauptdolomit of Upper Triassic age and underlain by the Wengener beds, also of the Upper Triassic, or by the Muschelkalk of the Middle Triassic.

The bauxite deposits of the Bihar Mountains in western Rumania are probably of Lower Cretaceous age. They occur as irregular sheets and lenses lying on the uneven surface of the Malm (Upper Jurassic) limestone. A thin bed of dark-colored limestone of Lower Cretaceous age immediately overlies the bauxite, and this is overlain by later limestones or by eruptive rocks. Locally the dark-colored limestone is absent.

Of approximately the same age as those of the Bihar Mountains are the bauxite deposits of Ariège in the northern part of the Pyrenees, France. These deposits are in the form of beds and lenses along the contact of Jurassic dolomite and overlying limestones of the Urgonian or Aptain (Lower Cretaceous).

The bauxite deposits of the Middle Cretaceous include those of southeastern France, central Italy, southwestern Montenegro, Greece, and perhaps, also, those of western Hungary.

The deposits of southeastern France extend discontinuously from Herault eastward through Bouches du Rhone and Var to within 50 or 60 miles of the Italian border. Wherever their geologic relation is evident, the deposits consist of beds or lenses usually lying on the eroded surface of limestones of Lower Cretaceous or Jurassic age.[1] In many places they lie on Urgo-nian (Lower Cretaceous) limestones, elsewhere on Neocomian rocks, and in still other places on rocks of the Malm (Upper Jurassic) or Lias (Lower Jurassic). The deposits are probably all older than Cenomanian (Middle Cretaceous), although Cenomanian limestones do not always form the capping rock, which may be Senonian or Danian (Upper Cretaceous) or even Eocene.

It seems, therefore, that the bauxites of southeastern France were probably formed during an erosion interval in Albian

[1] PAVLOVSKI, A., "Les Bauxites Françaises," Jules Charles et A. Bruner, Paris (1925).

(Middle Cretaceous) time and that they are probably residual products left by the decay of Albian, Aptian, and Urgonian limestones, and in some places, where weathering was very active, of Neocomian or Jurassic rocks. There is some question, however, whether sediments were deposited in early Albian time or whether lateritization extended throughout the Albian period. After the bauxite formation at the close of Albian time, submersion occurred and Cenomanian and younger limestones
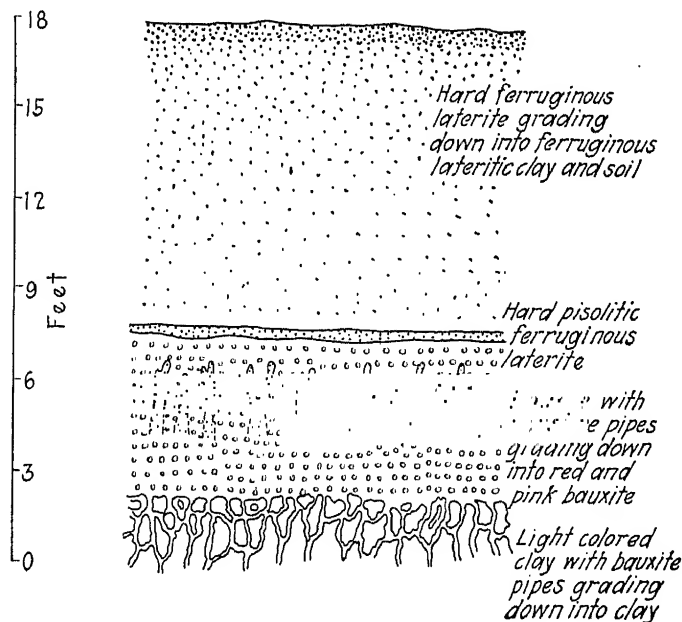

Fig. 19.   Section of ferruginous lateritic bauxite deposit in Brazil.

were deposited over the newly formed bauxite. That Cenomanian rocks are not universally present as capping rocks of the bauxite deposits is probably due, in part, to non-deposition and, in part, to removal during erosion periods subsequent to Cenomanian time.

The bauxites of the Apennines in central Italy occur east of Rome and north of Naples. They are in the form of beds and lenses associated with limestones of Cenomanian and Turonian age.

The bauxite deposits in the region between Kotor (Cattaro) and Niksic, southwestern Montenegro, occur as lenses and

irregular bodies underlain by Lower Cretaceous limestone and overlain by Middle Cretaceous limestone. Many of them are of considerable extent horizontally and protrusions extend from their lower surfaces into pockets in the underlying limestone.

The bauxite deposits of Greece are located on the Gulf of Corinth. They consist of layers and lenses underlain by Upper Jurassic limestone with nerinees and overlain by Upper Cretaceous rudistic limestone. The gap they occupy, therefore, embraces the middle and early parts of the Cretaceous period.

The Hungarian bauxite deposits occur north of Lake Balaton in a northeast-southwest belt that extends to within a short distance of Budapest. They were formed during the time interval between the deposition of the Dachsteinkalk or of the Hauptdolomit, both of Upper Triassic age, and the Eocene. They, therefore, occur in a hiatus that represents a very long geologic time interval embracing both the Jurassic and Cretaceous, and it is not possible to say whether they are related in age to the French bauxite of the Middle Cretaceous, or whether they should be referred to the Istrian and Dalmatian bauxite forming period of the early Eocene.

The bedded bauxite deposits of Lower Eocene age are widely distributed and present a great range in physical and chemical characteristics. They comprise the bauxites of Dalmatia, Herzegovina, and southern Montenegro in Yugoslavia, those of the Istrian Peninsula, Italy, those of the Barcelona region, northeastern Spain, the Jammu deposits of Kashmir, northwestern India, and the bedded bauxites of central and southern Georgia, southeastern Alabama, and northeastern Mississippi in the United States. Probably the bauxite deposits of central Arkansas are also of this period.

The principal bauxite deposits in Dalmatia and Herzegovina occur as lenses, usually underlain by alveoline limestone of Lower Eocene age and overlain by the "promina beds" of the Upper Eocene, consisting of thin bedded limestones and limestone breccias. In many places the alveoline limestone is absent and the bauxite lies directly on the rudistic limestone, the uppermost Cretaceous of this region. Although commonly the Yugoslavian deposits are in the form of interbedded lenses, in many places the upper surface of the underlying limestones has been rendered uneven by erosion and solution, and bauxite fills the pockets and solution cavities on this uneven surface. In

uch cases the bedded deposits grade into pocket deposits, vhich will be discussed later.

The bauxite of southern Montenegro occurs in the region of 3ar and Ulcinj. It is found as lenses and irregular bodies along he contact of the rudistic limestone and the overlying miliolid imestone (Eocene). There are also pocket deposits in the udistic limestone.

Most of the Istrian bauxite deposits are pocket deposits occuring in solution cavities in the rudistic limestone (Upper Cretaceous). Usually they are found at the surface or are covered by only a few meters of soil. In a few places, however, they are under several meters of Eocene beds, generally Nummulitic limetone. Their occurrence at or near the surface is in most places uc to the nearly horizontal Eocene rocks having been removed by rosion, leaving the bauxite exposed as lenses on the uneven surace of the underlying rudistic limestone and in pockets within it.

The bauxite of the Barcelona district occurs in the form of ockets and irregular lenses on the uneven erosion surface of 'riassic and Lower Eocene limestones. Cretaceous and Jurassic ocks are absent in the bauxite areas. The deposits are covered ith a thin layer of soil and no capping rocks are in evidence.

The bauxite layer of the Jammu district, India,[1] occurs at the ase of the Eocene. It is overlain by the Sabathu coal beds Eocene) and underlain by Jurassic limestone, from which it is parated, however, by a layer of siliceous breccia.

In southeastern United States, a belt of Eocene bauxite-bearing diments runs from central Georgia through southwestern eorgia and southern Alabama into northeastern Mississippi.[2]

[1] Fox, C. S., "The Bauxite and Aluminous Laterite Occurrences of adia," Mem. Geol. Survey India, 49, Pt. 1, 102 104 (1923).

[2] Cooke, W., "The Cenozoic Formations," in "Geology of Alabama," G. I. Adams, Chas. Butts, L. W. Stephenson, and W. Cooke, Geol. urvey Alabama, 251 297 (1926).

Rettger, R. E., "The Bauxite Deposits of Southeastern Alabama," on. Geol., 20, No. 7, 671 686, November, 1925.

Burchard, E. F., "Bauxite in Northeastern Mississippi," U. S. Geol. urvey Bull. 750-C (1925).

Morse, P. F., "The Bauxite Deposits of Mississippi," Mississippi ate Geol. Survey, Bull. 19 (1923).

Adams, G. I., "Bauxite Deposits of the Southern States," Econ. Geol. , No. 6, 615–620 (1927).

Shearer, H. K., "A Report on the Bauxite and Fullers Earth of the astal Plain of Georgia," Geol. Survey Georgia Bull. 31, pp. 123–132 (1917).

These sediments vary in character so that no single stratum can be readily followed throughout their extent. In Wilkinson County, Georgia, at the northeastern end of this belt, the bauxite deposits occur at the base of the Eocene. They overlie Lower Cretaceous clays and are overlain by sand and clay of Jackson age (Upper Eocene). To the southwest in Sumter and Macon counties, Georgia, the bauxite beds occur at or near the top of the Midway (Lower Eocene), being overlain by the Wilcox (Middle Eocene) clay and sand. In southeastern Alabama,

FIG. 20.—Loading bauxite at an Arkansas bauxite mine; material has been blasted preparatory to loading by steam shovel.

bauxite beds and lenses are associated with the Naheola formation, the uppermost member of the Midway group. The Naheola formation is overlain by Wilcox beds. In eastern Mississippi, the bauxite occurs at the top of the Porters Creek clay of the Midway group or at the base of the immediately overlying Ackerman formation of the Wilcox group.

These bauxites occur usually as moderately thin sheets of considerable horizontal extent and generally are underlain and overlain by clay. The contact with the overlying clay is usually quite sharp, while that with the underlying clay is gradational. Frequently the underlying clay is bauxitic clay, compact or

pisolitic. In a few places, as in southwestern Georgia and southeastern Alabama, the deposits are in pockets, probably because limestones that are associated with the clays underlying the bauxite horizon have by their solution formed an uneven surface.

The bauxites of the Eocene in Georgia and Alabama differ from the Eocene bauxites of Europe, in that they are usually white, low in iron oxide and high in combined water, while those of Europe are generally dark red, high in iron oxide and low in combined water. The bauxite deposits of Mississippi are of low grade, being high in silica and iron oxide.

The bauxite deposits of Arkansas occur in Pulaski and Saline counties, south and southwest of Little Rock. In this region there are intrusive masses of nepheline syenite, surrounded and in part overlain by Eocene (mainly Wilcox) clay and sand beds. Much of the bauxite occurs as a blanket on the uneven surface of the nepheline syenite masses and is covered by Eocene sediments. In a few places, layers or lenses of detrital bauxite occur interbedded with Eocene sediments.[1] (See Fig. 14.)

There are no important interbedded laterite deposits of later age than those of the Eocene but a few minor occurrences of impure bauxite, such as those of County Antrim, North Ireland, and those of the Vogelsberg Mountains, Germany, date from the middle or late Tertiary. It is possible also that some of the laterite blanket deposits previously described date back as far as the late Tertiary or early Quaternary but have no overlying sediments to indicate their age because they have not suffered submergence since their formation.

The main bauxite deposits of County Antrim[2] occur as irregular lenses or masses in the Interbasaltic Zone, a formation consisting of impure iron ore, bauxite, ferruginous clay and lithomarge, interlayered between the Upper and Lower Basalt of late Eocene or Oligocene age. One or more thin layers of similar material occur in the Lower Basalt. The bauxites are ferruginous and siliceous materials of low grade believed to be mainly the decomposition products of basalt. There are also, however, pale

[1] HAYES, C. W., "The Arkansas Bauxite Deposits," *U. S. Geol. Survey* 1 *Ann. Rep.* **111**, 437–472 (1901).

MEAD, W. J., "Occurrence and Origin of the Bauxite Deposits of Arkansas," *Econ. Geol.* **10**, No. 1, 28–54, January, 1915.

[2] COLE, G. A. J., "The Interbasaltic Rocks (Iron Ores and Bauxites) of North-East Ireland," *Mem. Geol. Survey Ireland* (1912).

siliceous bauxites, probably derived from the weathering of associated rhyolite flows.

The bauxite of the Vogelsberg Mountains[1] occurs in ferruginous clays derived from the decomposition of basalt flows of Upper Miocene age. For the most part it is in the form of nodules and fragments imbedded in terra rossa or variegated (chiefly red) clays. Brown iron ores in irregular segregations are abundantly associated with the bauxitic materials.

Pocket Deposits.

Pocket deposits of bauxite have been mentioned as occurring in association with certain interbedded bauxite layers and lenses. In this association they represent irregularities in the surface upon which the bauxite was formed. In many places bauxite pockets are directly connected with bauxite layers or lenses as extensions from their lower surfaces into cavities on the upper surface of the stratigraphically underlying rock, which is generally limestone. Elsewhere, the pockets are scattered irregularly or occur in groups, unconnected with bauxite layers or lenses, which, if they ever existed, have been removed by erosion. Such scattered pocket deposits are very abundant in Istria.

Besides pocket deposits in limestone, there are pocket deposits occurring in northwestern Georgia, northeastern Alabama, and eastern Tennessee, the geological relations of which are not so clearly defined. These pockets are found in clay in areas underlain by Cambro-Ordovician dolomite, and the clays which enclose them have generally been presumed to be residual clays derived from the decomposition of the dolomite. Many of the pockets, however, have associated with them masses of lignite or lignitic clay, which could not be residual from the Cambro-Ordovician dolomite, and this leads to the suspicion that perhaps some of the clays enclosing the bauxite are not residual but sedimentary clays, possibly of Tertiary age. The bauxite layers and lenses of central and southern Georgia and south-eastern Alabama are interbedded with Eocene clays, as already mentioned, and perhaps a somewhat similar relation exists between them and the north Georgia pocket deposits as exists between the bedded bauxite of the Adriatic region and the pocket deposits in limestone of Dalmatia and Istria.

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[1] HARRASSOWITZ, H., "Laterite, Material und Versuch erdgeschichtlicher Auswertung," Geb. Borntraeger, Berlin (1926).

The pocket deposits of bauxite of both types generally show
sharp contacts with the enclosing limestone and clay, but some
of the deposits in clay have walls of bauxitic clay high in alumina,
and such occurrences may be gradational, just as the bauxite
layers of central Georgia and southeastern Alabama sometimes
show a gradation into the underlying clay. The pocket
deposits in limestone in many places show knife-edge contacts
with the enclosing rock, but locally a thin cushion of terra rossa
(red earth) intervenes. The shape of both types of pockets is
irregular. Some of them are approximately equidimensional

Fig. 21.—Bauxite mine near Wriley, Georgia; upper surface of bauxite shown
by man's hat at left of picture.

but most of them are irregularly pod-shaped. The manner in
which they cut across the bedding of the enclosing rocks and
their arrangement in groups indicates the possibility that they
are fillings of solution caverns or caves. Adams has suggested
that the northeastern Alabama pocket deposits are sink-hole
fillings.[1] In some of the Istrian bauxite pockets, stalactites of
crystalline calcite are found locally along the walls.

Detrital Deposits.

Detrital bauxite deposits may occur in association with
bauxite deposits of any of the other types. They may be talus

ADAMS, GEO. I., "The Formation of Bauxite in Sink-holes," *Econ.
Geol.* **18**, 410–412.

accumulations on slopes below outcropping bauxite scarps, they may be stream gravels or sands, or they may be more or less continuous layers occurring either at the surface or interbedded with contemporaneous sedimentary rocks. In age they range from very recent surface accumulations, such as loose boulders below laterite outcrops in the tropics, to interbedded sedimentary accumulations of Tertiary age, as in Arkansas. In India, surface detrital accumulations of bauxite appear to be of considerable importance and many of them are old enough to have suffered a fair degree of consolidation. It is stated by Fox[1] that, in general, they are of higher grade than the original deposits from which their materials were derived.

ORIGIN OF BAUXITE AND LATERITE

The hypotheses that have been advanced to explain the origin of bauxite may be grouped under three main headings:

1. Chemical sedimentation.
2. Weathering in situ.
3. Detrital deposition.

In the past, many geologists have considered it necessary to explain bauxite deposits as originating by chemical sedimentation, thermal springs or springs highly charged with certain salts or acids being the agents of deposition. In recent years, however, the role of weathering processes in the formation of bauxite and related deposits has been more clearly recognized, and although even now some geologists believe that certain deposits are formed by chemical sedimentation, the general opinion is that most bauxite deposits are residual products resulting from the intensive weathering or lateritization of various rocks. Certain minor bauxite deposits are known to be of detrital origin, being the result of the mechanical concentration of bauxite fragments and particles derived by disintegration from previously existing bauxite deposits. A few geologists believe that even some of the more important bauxite deposits are of detrital origin.

Chemical Sedimentation.

The important bauxite deposits of southern United States, as well as those of France, although now generally considered to be

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[1] Fox, C. S., "The Bauxite and Aluminous Laterite Occurrences of India," *Mem. Geol. Survey India*, **49**, Pt. 1, 36-37 (1923).

ritic in character, have, in the past, been explained by a
nber of geologists as being the result of chemical sedimentation.
Coquand and Augé[1] believed that the French bauxite deposits
ulted from the action of hot springs and geysers in Cretaceous
es or estuaries. They assumed that hot springs supplied the
minum salts which were precipitated and were deposited
ng with other sediments.

. Meunier[2] had the opinion that salt waters penetrating
ough cracks into the earth and, becoming heated at a depth,
solved aluminum and iron from ferruginous and aluminous
ks in the form of chlorides. These waters, issuing from vents
the bottom of bodies of water in which calcareous sediments
'e being deposited, reacted with the calcium carbonate,
ming calcium chloride and depositing aluminum and iron
des.

. W. Hayes[3] in his study of the bauxite deposits of northern
orgia came to the conclusion that surface waters penetrating
considerable depths, particularly along fault planes, came in
tact with shales containing pyrite. The oxidation of the
ite he believed resulted in the formation of iron sulphate and
sulphuric acid, which upon being dissolved in the water,
acked the aluminum silicates of the shale, forming free silica
l aluminum sulphate. The aluminum sulphate in solution,
yes believed, on rising to the surface and coming into contact
h limestones would react with calcium carbonate, forming
ium sulphate and aluminum hydrate, the latter being
osited as a gelatinous precipitate.

n explaining the origin of the Arkansas bauxite, Hayes[4]
owed a line of reasoning similar to that used in the case of the
orgia and Alabama bauxite. He believed that the syenite
usions, while still hot, were acted upon by sea waters or

Coquand, M. H., "Sur les Bauxites de la chaîne des Alpines (Bouches du
ne) et leur âge géologique," *Bull. soc. geol. France*, 2nd Ser. **28**,
115 (1870–1871).

Augé, M., "Note sur la Bauxite, son origine, son âge et son importance
ogique," *Bull. soc. geol. France*, 3rd Ser. **16**, 345 (1888). Both authors
l by T. L. Watson.

Meunier, S., cited by R. Sylvany, "Bauxite," *Metal Ind.*, pp. 403–407,
e 30, 1916.

Hayes, C. W., Rome Folio, 78, Geologic Atlas of the United States.
S. *Geol. Survey*, 1902.

Hayes, C. W., "The Bauxite Deposits of Arkansas," 21st *Ann. Rep.*,
S *Geol. Survey*, Pt. 3, 441–472, 1901.

alkaline waters which became heavily charged with constituents of the syenite. Upon rising to the surface, these waters acted further upon the surface of the syenite, resulting in the leaching of silica, lime, and alkalies, leaving alumina and iron and depositing additional alumina which was taken into solution at depths. This alumina, he believed, in part, was deposited in place of the silica, lime, and alkalies removed and, in part, was precipitated on the surface of the syenite, forming a gelatinous deposit.

Later work by Adams[1] and Rettger[2] in Alabama and Georgia, and by Mead[3] in Arkansas, has resulted in developing more convincing hypotheses for the origin of these bauxite deposits than those proposed by Hayes (see pp. 94 and 96).

Recently, Shearer and Nelson have advocated the origin of bauxite deposits by chemical sedimentation. Shearer[4] believes that the bauxite deposits of the Georgia Coastal Plain are the result of hydrogen sulphide solutions acting on clay particles during sedimentation. The hydrogen sulphide originated by the action of free sulphuric acid on sulphides, the free sulphuric acid itself having been derived with sulphates by the action of oxidizing waters on disseminated pyrite in the rocks now underlying the bauxite deposits. The hydrogen sulphide solutions, finding an outlet in the beds of lakes or lagoons in which clay was being deposited, became oxidized, forming sulphuric acid which, attacking the clay particles, formed aluminum sulphate. The latter then became hydrolyzed by fresh hydrogen sulphide issuing from the springs and was precipitated as aluminum hydrate.

Nelson[5] concluded that the bauxite deposits of northwestern Georgia and eastern Tennessee were formed in swampy areas on a Pleistocene peneplain from solutions which derived their aluminum by the action of sulphuric-acid-bearing waters upon bentonite beds interlayed with Ordovician limestones of this region. Precipitation of aluminum hydrate, according to

[1] ADAMS, G. I., "The Formation of Bauxite in Sink-holes," *Econ. Geol.* **18**, 410–412 (1923).

[2] RETTGER, R. E., "The Bauxite Deposits of Southeastern Alabama," *Econ. Geol.* **20**, No. 7, 671–686 (1925).

[3] MEAD, W. J., "Occurrence and Origin of Bauxite Deposits of Arkansas," *Econ. Geol.* **10**, No. 1, 28–54, January, 1915.

[4] SHEARER, H. K., "A Report on the Bauxite and Fullers Earth of the Coastal Plain of Georgia," *Geol. Survey Georgia, Bull.* 31, 123–132 (1917).

[5] NELSON, W. A., "Appalachian Bauxite Deposits," *Bull. Geol. Soc. Am.*, **34**, 525–540 (1923).

elson, occurred by the action of tannic acid or other organic
ds in swamp waters when the aluminum-bearing solutions
ched the surface and mingled with these waters.

eathering in Situ.

In the weathering or decomposition of rocks at the earth's
rface, there is a gradual removal of the more soluble con-
tuents; alkalies, lime, and magnesia going first, followed later
silica, leaving iron oxides, titania, and alumina as relatively
soluble constituents. It is, therefore, natural that many
vestigators have come to the conclusion that normal weathering
ocesses are the dominant factors in the formation of bauxite,
rruginous bauxite, and aluminous iron-ore deposits. The
ceptance of this hypothesis is now so universal that the origin
practically all the more important bauxite deposits of the
orld is ascribed to surface weathering processes with solution
d redeposition of alumina and metasomatic replacement by
umina playing minor although locally important roles.

The abundant occurrence of bauxite and laterite in tropical
semitropical regions and its scarcity or complete absence
colder regions is probably due to the fact that the decom-
sition of rocks by weathering is most intensive and most com-
te in the former regions. In temperate and cold climates
sintegration becomes progressively more and more important
d decomposition less so. Even in the tropics, however, climatic
nditions vary widely in different localities from the arid con-
ions of the desert regions to the moist conditions of the rain
lts. These facts explain why bauxite and laterite deposits are
alized. Observers have noticed that lateritization is most
neral where there is a regular and distinct alternation of wet
d dry seasons.

Some investigators believe that the removal of soluble mate-
ls is the main factor in the accumulation of residual insoluble
k constituents into laterite and bauxite. Others believe that
me solution of even the more insoluble substances occurs and
at their subsequent redeposition in pores and cavities is of
portance in the formation of bauxite deposits. Organic
encies, such as bacteria, are believed to assist in the breaking up
d dissolving of the original minerals. Metasomatic replace-
nt is mentioned as one of the important processes in the
eration by weathering of original aluminum-bearing rocks

to laterites.   It is probable that all of these processes are involved
to a greater or less degree in lateritization or bauxitization.

One of the first investigators to show the true nature of
laterite was Bauer.[1]   He demonstrated, after a careful exam-
ination of laterite specimens from the Seyschelles Islands, that
this laterite, consisting largely of a mixture of gibbsite and
hydrated iron oxides with or without quartz, retained the
texture of the original granite, diorite or diabase, and appeared
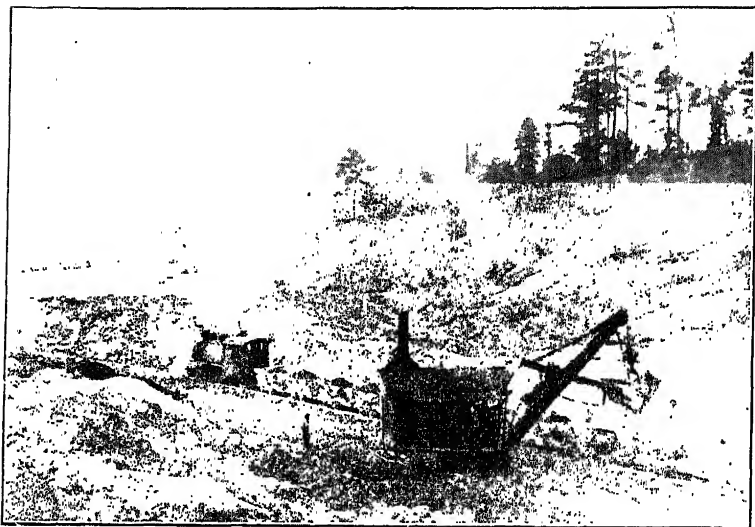
FIG. 22.—Loading bauxite by steam shovel in Arkansas.

to be formed by the alteration in place of the original aluminum
and iron silicates to aluminum and iron hydrates, accompanied
by the removal of silica.   Microscopic examinations showed
that the outlines of the original feldspars, amphiboles and pyrox-
enes still existed in the laterite, but that their interiors consisted
of fine scaly aggregates of gibbsite, with perhaps some diaspore,
stained along cracks and cleavage planes by infiltrations of
hydrated iron oxides.   Quartz where present in the original rock
persisted in the resulting laterite.   Bauer noted the great
similarity between the laterite of the Seyschelles Islands and the
bauxite of the Vogelsberg Mountains, and in both cases he

[1] BAUER, M., "Beiträge zur Geologie der Seyschellen, insbesondere zur
Kenntnis des Laterits," *Neues Jahrb.*, **11**, 163–219 (1898).

considered their formation as the result of leaching, the bauxite or laterite being left as residue.

Holland[1] mentions the possibility of bacteria being instrumental in the deposition of aluminum oxides in the lateritic blanket deposits of India.   He suggests that some low forms of life might have the power of separating alumina and using it in their life processes, their growth or their protection, just as calcium carbonate, silica, and iron oxide are used by organisms.   However, his suggestions do not appear to have been based on detailed observations or experiments.

Maclaren[2] accounts for the formation of laterite blankets by the gradual solution of silica and other substances and the deposition in place of them of iron oxide and aluminum hydrates. He is of the opinion that laterite or bauxite, instead of being a direct residual product of weathering, is rather a replacement of such a residual product.   He believes that the solution of the requisite materials is accomplished by carbonate solutions and that deposition occurs under the influence of successive saturation and dessication resulting from slow movement upward and downward of the water table as a result of regularly alternating wet and dry seasons.   It is in this surface zone of alternating wetness and dryness that Maclaren believes the laterite and bauxite formation takes place.   The movement, he believes, is mainly through capillary openings and the alternate solution and deposition takes place in the walls of these same openings, resulting in the concentration of the less soluble materials constituting the laterite.

Campbell,[3] after a study of lateritization in French Guinea, gives the following conditions most favorable to the formation of laterite, (a) alternating wet and dry seasons, (b) a pronounced dry season, provided enough rain falls during the wet season for abundant vegetation, (c) luxuriant vegetation and tropical temperature, (d) fluctuating water level not far from the surface, (e) gently sloping surface of the ground.

Campbell believes that the process of lateritization involves a solution of the more soluble materials during the downward

[1] HOLLAND, T. H., "The Constitution, Origin, and Dehydration of Laterite," *Geol. Mag.*, Decade IV, **10**, 59–69 (1903).

[2] MACLAREN, M., "On the Origin of Certain Laterites," *Geol. Mag.*, Decade V, **3**, No. 12, 536–547, December, 1906.

[3] CAMPBELL, J. MORROW, "The Origin of Laterite," *Trans. Inst. Mining Met. Eng.*, **19**, 432–443 (1909–1910).

passage of surface water, thus causing a relative enrichment of the less soluble materials, such as aluminum hydrates and iron oxides, in the surface layers.   In addition to this, he believes that certain of the less soluble constituents which are dissolved in the downward passage of the water, including both aluminum and iron compounds, are redeposited at or near the level of the water table.   Thus there is lateritization by the removal of non-lateritic materials in the upper part of the surface zone, as well as by the precipitation of lateritic materials in the lower part of the surface zone.

Veatch,[1] one of the first to study the bauxite deposits of the Georgia Coastal Plain, believes that they are derived by the desilication of clay, through the action of alkaline carbonates or bicarbonates, such as $NaHCO_3$, leaving aluminum hydrates as a gelatinous residue.   He suggests that the alkaline solutions were derived by the action of carbonic acid on alkaline silicates or other alkaline salts in the overlying Tertiary sediments.

Fermor,[2] although he refrains from discussing the origin of laterite, indicates in his classification that he believes laterite may form as detrital deposits, as chemical sediments, and by metasomatic replacement, but that "true laterites" are the result of weathering in situ and the removal of the more soluble constituents.

Arsandaux[3] makes a comparison between the laterites of the Sudan and the Congo and the bauxite of southern France.   In the case of the tropical laterites, he believes that the alteration is the result of hydration of the original aluminum and iron silicates.   The aluminum silicates, he believes, are altered first to hydrous aluminum silicates which gradually change to kaolinite, and this in turn probably to aluminum hydrate.   The iron silicates upon hydration are altered to ferric hydrates.   As regards the French bauxite, he finds that in the ordinary varieties the aluminum is present as aluminum monohydrate but that in the siliceous varieties there is a tendency to a slightly higher combined water content than is required by the monohydrate.

[1] VEATCH, O., Report on the Bauxite Deposits of Wilkinson County, Georgia, *Geol. Sur. Georgia, Bull.* **18**, 430–447 (1909).

[2] FERMOR, L. L., "What is Laterite?" *Geol. Mag.*, Decade V, **8**, October, November, December, 1911.

[3] ARSANDAUX, H. M., "Contribution a l'étude de l'altération des roches silicatees-alumineuses dans les régions inter-tropicales," *Bull. soc. franç. minéral.*, **36**, 70–110 (1913).

He finds further that the iron is mainly present as hematite with very little ferric hydrate. He believes that the low water content of the French bauxite, as compared with tropical laterite, is probably due to conditions, possibly climatic, subsequent to their formation.

Lacroix,[1] in discussing the formation of the laterite in French Guinea, notes the occurrence of two zones of lateritization, the lower or zone of leaching (zone de départ) and the upper or zone of concretion (zone de concretion). The two zones grade into each other, the action begun in the one being continued without break into the other, the main difference being that in the lower zone much of the original rock texture is retained, whereas, in the upper, the original texture is almost obliterated. The lower zone is characterized by the elimination of most of the more soluble constituents, whereas the upper zone is characterized by the migration of iron oxide upward to form a surface crust, generally with pisolitic texture, and by a tendency of the iron oxides and aluminum hydrates to segregate. He mentions three groups of rocks that react differently in the two zones (1) diabase, gabbro, and nepheline-syenite that give rise in the zone of leaching, with abrupt change and without transition, to gibbsitic laterite, which latter, in the zone of concretion, suffers segregation of iron oxides and segregation and recrystallization of aluminum hydrates; (2) peridotite that is altered in the zone of leaching to porous, ocherous, ferruginous laterite, which in the zone of concretion changes to a variety of concretionary forms of limonite and its colloidal equivalent stilpnosiderite with partial dehydration to hematite; (3) mica schist, gneiss, and granite, which in the zone of leaching change very gradually to clayey alteration products, so that the zone is very thick, becoming richer in colloidal hydrates in the upper portion. The change continues in the zone of concretion, resulting in the formation of bauxitic laterites, commonly with pisolitic texture, in contrast to the crystalline texture of gibbsitic laterites. While the above is given as the general mode of alteration of the rocks mentioned, there are exceptions. Thus he mentions the occurrence in many places of clay as well as of gibbsitic laterite as an alteration product of nepheline syenite. Lacroix states his belief that bauxitic pisolites are concretionary

[1] LACROIX, A., "Les Latérites de la Guinée et les Produits d'altération," *Nouv. Arch. du Mus.*, 5, Paris, (1913).

textures developed in place and not the result of chemical deposition.

In lateritic alteration much significance is attached by Lacroix to the change from feldspar to aluminum hydrate, the latter occupying in many places the original outlines of the feldspar. Such a change, however, may not be strictly an alteration in place, there being probably a certain amount of transfer, rearrangement, and replacement of materials. This, however, is more particularly true of the iron in its change from ferrous and ferric silicates to hydrated oxides and oxides.

Mead,[1] who made a study of the Arkansas bauxites, concludes that they were formed by subaerial weathering processes, rather than by the action of heated waters, as suggested by Hayes (see p. 87). He makes the following brief statement of their origin:

Large masses of nepheline syenite were intruded into folded Paleozoic rocks and subsequently exposed at the surface by erosion. The bauxite deposits were developed on the undulating surface of the syenite by weathering, and suffered considerable contemporaneous erosion by streams. The entire area was then covered by terrestrial sediments of probable Tertiary age and consisting of clays, sands, and gravels with lenses of lignitic material. The syenite areas, being more resistant to erosion, stood in relief above the surrounding areas of softer rocks on the Tertiary land surface, and the bauxite deposits suffered erosion contemporaneous with the deposition of the lower Tertiary sediments, resulting in the transportation of bauxite and its interstratification with sands and gravels around the border of the syenite area and in topographic depressions within it. Recent erosion has cut through the Tertiary sediments exposing the underlying igneous rocks and the bauxite deposits.

Mead states that "the bauxite and associated clays are the products of surface weathering of the syenite by normal processes of rock decomposition, and are in no sense chemical sediments." The deposits on the surface of the syenite have developed in situ from the syenite. This rock, Mead believes, altered first to clay which was very porous as a result of the removal of much readily soluble material. On account of the porous nature of the clay, he believes it was then further altered to bauxite under tropical or subtropical conditions by the removal of silica.

[1] MEAD, W. J., "Occurrence and Origin of Bauxite Deposits of Arkansas," *Econ. Geol.* **10**, No. 1, 28–54, January, 1915.

The deposits also suffered downward secondary enrichment of alumina, shown by the fact that the upper crusts are higher in silica than the main body of the bauxite, and by the presence of gibbsite veins in the latter.

As regards the bauxite lenses interlayered with Tertiary sediments, Mead believes that they consist of material from the original deposits which has been redeposited by Tertiary streams. These deposits, as well as the upper portions of the original deposits, consist of oolitic or pisolitic bauxite, and he believes that this texture has developed in place from the original granitic

Fig. 23.—Opening up a new deposit, British Guiana, showing small amount of overburden being stripped by mule carts and cleaned bauxite face ready to mine.

or amorphous texture. Mead's hypothesis is well supported by field evidence.

Beyschlag,[1] in discussing the structure and origin of the bauxite in the Bihar Mountains of Rumania, comes to the conclusion that it originated in situ by lateritic weathering of limestone deposited on a former sea bottom that became land at the end of Jurassic time. He believes it was formed by the solution and removal of the calcium carbonate and the simultaneous concentration of the alumina, iron oxide, and silica originally present, without other additions.

[1] Beyschlag, F., "Bauxit Vorkommen des Bihar Gebirges," *Z. deut. geol. Ges.* **70** 10 (1918).

Adams[1] discards Hayes' hypothesis of the origin of the Appalachian bauxite deposits of northwestern Georgia and northeastern Alabama by chemical deposition (see p. 87), and suggests that they are probably alteration products of clay accumulations in sink-holes. This belief is based on the pocket-like form of the deposits and on the association with the bauxite of lignite and limonitic iron ore.

Rettger[2] disagrees with Shearer in regard to the origin of the bauxite deposits of the Georgia-Alabama Coastal Plain region

FIG. 24.—Same deposit as shown in Fig. 23 after several months' mining.

(see p. 88) and believes that they originated by the surface weathering of sedimentary clays. He thinks the clays were deposited in lagoons, lakes, and shallow coastal waters, after which the land was slightly elevated so that it existed as fairly low, flat plain. The upper portions of the clay deposits were then exposed to weathering without being subject to immediate removal by erosion. The temperature, Rettger believes, was extremely mild. He says:

Under these conditions the clay was altered to bauxitic clay and bauxite by the removal of silica and the addition of water. The

[1] ADAMS, G. I., "The Formation of Bauxite in Sink-holes," *Econ. Geol.* **18,** 410–412 (1923).

[2] RETTGER, R. E., "The Bauxite Deposits of Southeastern Alabama," *Econ. Geol.* **20,** No. 7, 671–686 (1925).

altering solutions are supposed to have been those ordinarily present at the surface, such as carbonic acid or humic acid, . . . or possibly sulphuric or nitric acids.

Kitson,[1] who has made a study of the laterite deposits of the Gold Coast, gives as his opinion that they have been formed "from clay shales by the natural abstraction of silica, thus converting the hydrated silicate of alumina (clay) into aluminum hydrate (bauxite)." He finds irregular tubes of bauxite extending into the clay underlying the laterite capping and believes that water charged with dissolving agents percolates downward along these tubes, "decomposing the clay, bearing away the silica, and leaving the alumina." He believes the dissolving agents to be "carbon dioxide, and perhaps humic acid, derived probably from decaying vegetation." Kitson thinks that the iron oxide may have been added after the formation of the bauxite.

Harrassowitz,[2] after a careful study of the literature on laterite and bauxite, as well as original work on the bauxite of the Vogelsberg Mountains and elsewhere in Europe, divides the lateritic blanket deposits into several horizontal zones similar to those of Lacroix. At the base is the fresh rock. This is overlain by the "zone of decomposition," in which the original aluminum silicate minerals have altered to siallite (hydrous aluminum silicates) with usually the retention of the original rock texture. This grades upward into the "mottled zone," where allite (aluminum hydrate) formation takes place and the original rock texture disappears. At the top of the laterite blanket is the iron crust, porous and cellular, with enrichment by iron compounds, alumina and silica gels, and aluminum hydrate. Not all of these zones are everywhere present. Locally, the fresh rock may alter directly to allite and then the siallite zone is absent. Elsewhere, the iron crust may be absent or both the iron crust and the allite zone may be missing.

According to Harrassowitz, lateritization consists in the removal in solution of the bases, such as the alkalies and alkaline earths, and more gradually of silica, leading to the formation

[1] KITSON, A. E., "Outlines of the Mineral and Water Power resources of the Gold Coast, British West Africa." *Gold Coast Geol. Survey, Bull.* **1**, 16–34 (1925).

[2] HARRASSOWITZ, H., Laterit, Material und Versuch erdgeschichtlicher Auswertung. Geb. Borntraeger. Berlin (1926).

of siallite and then allite. Alumina, he believes, is also in part soluble and some of it, as well as some of the iron and the silica that have not been carried away, takes part in a movement in solution upward through the laterite blanket during the dry season. This leads to a gradual enrichment of the upper zones in iron oxide and alumina at the expense of the lower. Cellular and pisolitic textures develop in the upper zones owing to the influence of various gels in the solutions.

Fox[1] calls attention to the regular occurrence in many surface laterite deposits of three layers: (*a*) an upper red or brown crust, very high in iron oxide, (*b*) a middle layer, mainly bauxite, and (*c*) a lower layer of laminated lithomarge.

He believes that during the rainy season the rain water carrying acids or salts, percolating down through the laterite layer and issuing as springs below the laterite scarps, carries much soluble and finely suspended siliceous matter. The former is probably removed and the latter may be deposited as lithomarge. After the close of the rainy season, he believes that capillary action would cause ferruginous waters to move to the surface from small depths, and this would result in a deposition of limonite to form a surface iron crust. With the removal of the iron upward and the silica downward, the intermediate portions of the zone would gradually become bauxite. The removal of silica is somewhat difficult to explain and Fox believes that in part it may be due to electrokinetic phenomena and to the complete breaking down of silicate minerals into component sols and gels.

The steady flow of water (electrolyte) down through the porous mass of decomposed rock, the induced electric-potential difference between the top and bottom of this porous zone of decomposed rock and the presence of colloidal, electrically charged particles (sols and gels), supply all the electrokinetic conditions which are necessary in addition to the removal by solution and in suspension and upward capillarity . . . for a complete separation of the various constituents. The aluminum hydrogels will remain practically stationary and function in the porous zone as an impermeable membrane. The positively charged ferric hydrogels will be actuated upward both by capillarity and under electrical attraction of the electrical (negative sign) potential of the upper part of the laterite zone. The negatively charged silica in gel or sol form will be influenced downward both by the down-

[1] Fox, C. S., "Bauxite," 80–85, Crosby Lockwood & Son, London (1927).

ward current of water and under the electrical draw from the positively charged electrical potential in the lower layer. The neutral hydrous silicate compounds will gravitate in suspension with the relatively rapid downward flow of the percolating water and be precipitated where the velocity is greatly reduced, *i.e.*, at the base of the laterite mantle.

Recently Thiel,[1] by a series of experiments, has shown the effectiveness of sulphate-reducing bacteria in breaking up aluminum silicates and taking the aluminum into solution in the form of aluminum sulphate or, if iron is present, in the form of a double sulphate of iron and aluminum. Thiel believes that the home of the sulphate-reducing organisms is in the thin layer of clayey or loamy soil that overlies the bauxite. These organisms have the power of taking oxygen from sulphates, sulphites, and thiosulphates, thus reducing them to sulphides. The sulphides (mainly of iron) become oxidized by surface water, producing sulphates and sulphuric acid and the latter reacting upon aluminum silicates produces aluminum sulphate and free silica. The aluminum sulphate is hydrolyzed in its downward passage and yields aluminum hydrate.

The presence of sulphate-reducing organisms is not necessary for the above reactions, as the same results would be obtained from oxidation of natural iron or other sulphides. Natural sulphides are probably not as universally present in surface soils, however, as are sulphate-reducing organisms.

Detrital Deposition.

Formation of detrital deposits of bauxite presupposes the existence of earlier bauxite deposits formed by this or some other process. Hypotheses of detrital or clastic origin have for the most part been advanced in explanation of minor occurrences in bauxite fields where the principal deposits are described as originating either by chemical sedimentation or by weathering in situ. Some geologists, however, have advocated a wider application of the hypothesis of detrital sedimentation and among those are Lacroix, Kispatic and more recently, Malyavkin.

Lacroix,[2] in discussing the origin of the bauxite deposits of southern France discards the hypothesis of chemical sedimentation

[1] THIEL, GEORGE A., "The Enrichment of Bauxite Deposits through the Activity of Micro-organisms," *Econ. Geol.* **22**, No. 5, 480–493, August, 1927.

[2] LACROIX, A., "Minéralogie de la France et de ses Colonies," **3**, 342, (1901).
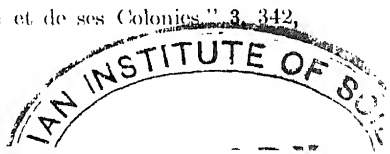
of the earlier French geologists and advocates a lateritic origin.
He suggests that the weathering of silicate rocks gave rise to
aluminous and ferruginous lateritic materials, which were depos-
ited as lenses and beds on a Jurassic and early Cretaceous
limestone surface and later suffered submersion and were covered
by late Cretaceous limey sediments.

Kispatic[1] has examined microscopically bauxite and terra
rossa of Croatia, as well as limestone and dolomite with which
they are associated, and finds the same accessory minerals in all

Fig. 25.—Dalmatian bauxite mine. This particular pocket has been almost
completely mined out. Light colored rock is limestone.

of them. He also finds that the limestone and dolomite contain
aluminum hydrates, mainly $Al_2O_3.H_2O$, as fine particles in the
amorphous form, which he terms "sporogelite." He believes
that the present bauxite deposits of the Adriatic region and the
associated terra rossa represent accumulations of residual
material from limestone and dolomite decay, mainly sporogelite,
which has been transported a greater or less distance and has
been more or less reworked and sorted.

Kerner von Marilaun,[2] in reviewing Kispatic's hypothesis
regarding the origin of Croatian bauxite, calls attention to the

[1] KISPATIC, M., "Bauxite des kroatischen Karstes und ihre Entstehung,"
Neues Jahrb. **34**, 513-552 (1911).

[2] KERNER VON MARILAUN, F., "Geologie der Bauxitlagerstäten des
südlichen Teiles der Osterreichisch-Ungarischen Monarchie," Berg- und
Hüttenmänn Jahrb. 139-170 (1916).

fact that the iron, silicon, and a certain portion of the aluminum are present in the original limestone and dolomite, not as oxides but as carbonates and silicates; and that, therefore, in addition to the mechanical accumulation of limestone residues into bauxite deposits there must be a certain amount of decomposition of carbonates and silicates by weathering.

Malyavkin[1] has advanced the hypothesis of clastic sedimentary origin for the laterite beds and lenses of the Tikhvin district, Russia. He believes that the laterite from which these were derived originally existed in the pre-Cambrian region of northern Russia, having resulted from the weathering of feldspar-bearing igneous rocks. No trace of the original laterite has been found, however, and it seems questionable if laterite materials could be transported over long distances and redeposited without losing their identity by admixtures of other clastic materials. Perhaps it would be more simple to explain these deposits as the residual products in place resulting from the lateritization of Lower Carboniferous or Devonian clays.

The geologists who explain minor occurrences of bauxite in certain fields as originating by the breaking up and reworking of bauxite from more important original deposits in the same field are Mead and Fox.

In Arkansas the principal deposits are described by Mead[2] as consisting of residual material derived from the weathering of nepheline syenite, while certain minor occurrences in the form of lenses interlayered with Tertiary sediments are described as being derived by the mechanical breaking up of parts of the main deposits and the redeposition of the materials as sedimentary beds in nearby shallow waters.

In India certain low-level bauxitic laterites, or laterites occurring on slopes, are described by Fox[3] as being detrital deposits formed by the mechanical disintegration of primary residual laterites capping plateau areas, and the transportation and migration of such broken materials down the slopes.

Thus detrital bauxite deposits may accumulate under water, as was probably the case in Arkansas, or they may be of subaerial

[1] MALYAVKIN, S. F., "Boksit." *Bull. acad. sci., U. S. S. R.* pp. 145-178 (1926).

[2] MEAD, W. J., "Occurrence and Origin of the Bauxite Deposits of Arkansas," *Econ. Geol.* **10**, No. 1, 28-54, January, 1915.

[3] FOX, C. S., "The Bauxite and Aluminous Laterite Occurrences of India," *Mem. Geol. Survey India*, **49**, Pt. 1, 36-38 (1923).

origin as in India.   In many places they have been consolidated subsequently to their deposition so that they are practically as solid as the original deposits from which they were derived.   In part this is due to compression and in part to cementation by solution and redeposition or replacement.   Consolidated detrital laterite is in many places difficult to distinguish from original laterite formed in situ and, according to Fox, original lateritization in situ occurs in places on the surface of the rock underlying detrital laterites.

Conclusions.

From the foregoing discussion, it will have been noted that, in the past, there has been much difference in opinion as to the origin of bauxite and laterite, but that there has been a general tendency, especially in late years, to regard them as the products of rock decomposition by weathering.   This is partly the result of much careful study of the structure of bauxitic laterite deposits of recent origin or actually still forming, and their comparison as regards composition, texture, and geologic relations with older bauxite deposits, and partly the result of a geological study of the older bauxite deposits and their relations to the enclosing rocks. Moreover, a large amount of research and study has been devoted in the past twenty years to the disintegration and decomposition of rocks and the formation of soils.

Perhaps the most striking characteristic of recent laterite deposits is their occurrence on flat or gently undulating surfaces which are without doubt remnants of former peneplains.   Similarly, the most striking characteristic of older laterite and bauxite deposits is their relation to geologic unconformities, suggesting their formation during past erosion periods and probably on former peneplains or base-leveled surfaces.   Thus, the inference is that bauxite deposits are formed on flat or gently sloping surfaces that have been exposed for long periods to decomposition by weathering and on which the mechanical removal of materials has been at a minimum.

The more exact conditions under which laterite is formed, such as the chemical processes and reactions involved in lateritization, have received much study but are far from being satisfactorily explained.   There is disagreement as to whether the solution and removal of the bases and silica, leaving alumina and iron oxides as residues, are the more important processes, or

whether these are exceeded in importance by the solution of alumina and iron oxide and their redeposition by metasomatic replacement or as fillings in openings.

There is much speculation as to the nature of the solutions that cause lateritization and as to the changes that occur in such solutions during the lateritization processes. It is known that carbonated alkaline waters take silica into solution, leaving
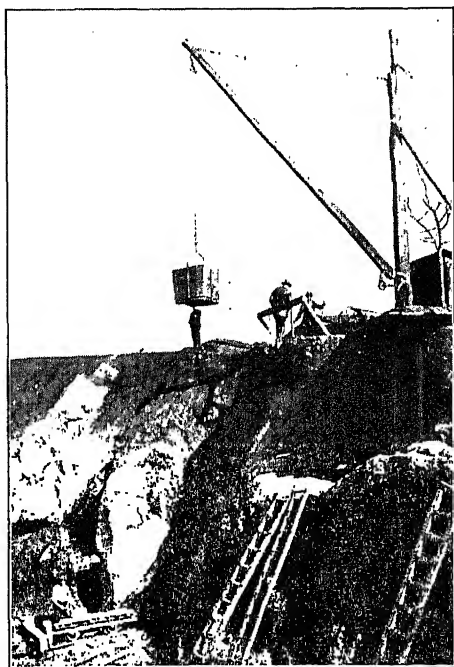
Fig. 26.- Bauxite mine in Istria. Dark colored material is bauxite; lighter material is limestone. The picture shows pockety type of Istrian bauxite deposits.

alumina and iron oxides behind, and it is known that acid waters, particularly solutions of sulphuric or nitric acid, dissolve aluminum and iron compounds and retain them in solution until the nature of the solution changes so that precipitation takes place. Moreover, organic acids resulting from the decay of vegetable matter are mentioned by some investigators as solvents and by others as precipitants.

There is disagreement as to the nature of rock alteration during lateritization. Some investigators, cognizant of the fact

that direct alteration of feldspar and other aluminum silicates to aluminum hydrates occurs, believe, nevertheless, that there is usually first an alteration of the original aluminum silicates to hydrous aluminum silicates, such as various clay minerals, and then a further alteration of the latter to aluminum hydrates. Other investigators believe kaolinization and lateritization to be two entirely distinct processes; the former the result of normal weathering and the latter occurring under special conditions and circumstances. They believe that kaolin and laterite both form directly from the original rock and that the clays so frequently intervening between the bed rock and the bauxite or laterite, such as the porous clay in Arkansas, the terra rossa in southern Europe, and the lithomarge in India, show a change in climatic or other conditions arising from the discontinuance of lateritization and the substitution of kaolinization.

In spite of the uncertainties and disagreements, and although little is known of the chemistry of lateritization, present knowledge indicates that laterites, bauxites, and lateritic iron ores are the end products of rock decomposition by weathering, and that they are usually formed under tropical or subtropical conditions of alternating dry and rainy seasons during long periods of quiescence when the land has been base leveled.

OCCURRENCE AND PRODUCTION OF ALUMINUM ORES

Although bauxite and laterite occur abundantly in many parts of the world, the present (1929) mining of aluminum ores in important quantities is confined to a few countries.

The chief bauxite-producing districts in the order of their present rate of production are as follows:

1. Var, Southern France.
2. Arkansas, United States.
3. Dutch Guiana, South America.
4. Western Hungary.
5. British Guiana, South America.
6. Istrian Peninsula, Italy.
7. Dalmatia, Yugoslavia.
8. Herault, Southern France.
9. Georgia-Tennessee-Alabama Field, United States.

The producing districts of minor or intermittent importance are:

1. Central Apennines, Italy.
2. Gulf of Corinth, Greece.
3. Ariege, Southern France.
4. Bouches du Rhone, Southern France.
5. Central Provinces, India.
6. County Antrim, Ireland.
7. Bihar Mountains, Rumania.
8. Victoria, Australia.
9. Central Missouri, United States.
10. Vogelsberg Mountains, Germany.
11. Barcelona, Spain.

Table 4 shows the annual production of aluminum ore in the various producing countries from 1920 to 1928, inclusive.

TABLE 4.—World's Production of Bauxite 1920–1928 Inclusive, by Countries, in Long Tons

(Statistics from U. S. Bureau of Mines, unless otherwise indicated)

Country	1920	1921	1922	1923	1924	1925	1926	1927	1928
Australia, Victoria								921	(a)
Austria	356	2,506	4,030	2,691	3,000(d)	4,000(d)	5,000(d)	1,781(c)	6,314(c)
Bulgaria					783			(a)	(a)
France	221,923(e)	131,745(e)	147,163(e)	354,313(e)	374,568(e)	400,273(e)	401,552(e)	531,368(e)	589,245(e)
Germany	13,208	9,962	14,911	6,559	3,036	1,739		2,362	(a)
Guiana, British	31,379(c)	90	(b)	100,346(c)	154,323(c)	174,999(c)	186,114(c)	160,872(c)	165,422(c)
Guiana, Dutch			18,508	15,589	62,100	84,914	43,531	177,836	203,459(f)
Greece					1,279	3,641	2,283	1,279	(a)
Hungary	6,300	6,652		492	189	384	3,608	283,403(g)	179,350(g)
India, British	11,020	2,268	4,919	6,547	23,227	10,070	4,956	(a)	(a)
Ireland, Northern	12,931		5,859	3,449	5,158	5,040	5,905(h)	5,309	(a)
Italy	(a)	48,344	65,593	96,506	138,565	191,919	89,070	93,794	157,440(i)
Rumania	531		3,678	4,096			733	1,679	(a)
Spain		181							(a)
United States	521,306	139,550	309,599	522,688	347,568	316,538	392,249	320,939	364,940
Yugoslavia	18,815(j)	9,863	30,796	26,157(j)	18,193	77,783	129,745	98,742	48,473(k)
	837,769	351,161	605,053	1,139,433	1,131,989	1,271,300	1,264,746	1,680,285	1,714,643

(a) Data not available.

(b) Early in 1921 operations at the bauxite mines were discontinued and the mines remained closed until late in 1922. Shipments were made from stocks in 1921. No shipments were made in 1922.

(c) Exports.

(d) "Mineral Industry," McGraw-Hill Publishing Company, Inc., New York (estimated).

(e) French National Statistical Bureau.

(f) Suriname Government Statistics.

(g) Budapest Chamber of Commerce.

(h) "Mineral Industry," McGraw-Hill Publishing Company, Inc., New York.

(i) Statistical Bureau, Royal Mining Administration, Rome.

(j) Belgrade Chamber of Commerce.

(k) Bureau of Mines, Split.

The following table shows the production, imports, and exports of aluminum ore in the United States since the beginning of the industry:

TABLE 5.—BAUXITE PRODUCED IN, IMPORTED INTO, AND EXPORTED FROM THE UNITED STATES, 1889 TO 1928 INCLUSIVE, IN LONG TONS
(From U. S. Geological Survey)

Year	Georgia	Alabama	Tennessee	Arkansas	Total	Imports	Exports[1]
1889	728				728		
1890	1,844				1,844		
1891	3,301	292			3,593		
1892	5,110	5,408			10,518		
1893	2,415	6,764			9,179		
1894	2,050	9,016			11,066		
1895	3,756	13,313			17,069		
1896	7,313	11,051			18,364		
1897	7,507	13,083			20,590		
1898					25,149	1,201	
1899	15,736	14,499		5,045	35,280	6,666	
1900	19,739			3,445	23,184	8,656	
1901	18,038			867	18,905	18,313	
1902	22,677			4,645	27,322	15,790	
1903	22,374			25,713	48,087	14,889	
1904	21,913			25,748	47,661	15,374	
1905	15,173			32,956	48,129	11,726	
1906	25,065			50,267	75,332	17,809	
1907	34,271		63,505		97,776	25,066	
1908	14,464		37,703		52,167	21,679	
1909	22,227		106,874		129,101	18,688	
1910	33,096		115,836		148,932	15,669	
1911	30,170		125,448		155,618	43,222	
1912	19,587	14,173	8,806	117,299	159,865	26,214	
1913	27,409		12,961	169,871	210,241	21,456	
1914	18,547		5,524	195,247	219,318	24,844	5,374*
1915	25,008		3,237	268,796	297,041	3,120	16,082
	Georgia, Alabama and Tennessee						
1916	19,190			375,910	425,100	30	17,939
1917	62,134			506,556	568,690	7,691	21,791
1918	42,829			562,892	605,721	3,653	19,711
1919	43,076			333,490	376,566	6,082	17,701
1920	40,029			481,279	521,308	42,805	22,257
1921	14,700			124,850	139,550	27,587	5,942
1922	42,810			266,790	309,600	23,656	19,617
1923	28,810			493,880	522,690	119,020	78,560
1924	19,940			327,630	347,570	201,974	77,065
1925	20,220			296,320	316,540	353,696	78,633
1926	20,680			371,570	392,250	281,644	87,770
1927	17,110			303,830	320,940	356,580	121,858
1928	14,190			361,236	375,426	350,111	112,984

[1] Includes bauxite concentrates

* Figures cover six months, July to December, 1914.   Not separately classified by Bureau Foreign and Domestic Commerce prior to July, 1914.

France.

Southern France, including the Var, Bouches du Rhone, Herault, and Ariège districts, has been the world's largest annual producer of bauxite, except for a few years during and following the World War when the French production was exceeded by that in the United States. The Var district has been the most important, and recently it has yielded annually nearly 80 per cent of the bauxite produced in France, while Herault has yielded about 15 per cent, the remainder being divided about equally between Ariège and Bouches du Rhone. The principal mines of the Var district are in the Brignoles region, including the mines near Le Luc, Le Thoronet, Cabasse, Vins, Le Val, Tourves, St. Maximin, Mazaugues, and La Celle. There are also important mines in the region of Tavernes and in the vicinity of Toulon. In Herault the principal producing mines are in the neighborhood of Villeveyrac, Loupian, St. Chinian, Cette, Beziers, and Bedarieux; in Bouches du Rhone near Parizot and near Les Baux, from which latter district bauxite derives its name, and in Ariège from the areas near Foix and St. Girons.

French bauxite is to a very large extent refined in southern France, there being plants, where alumina and aluminum hydrate are produced, at St. Auban in Basses Alpes, at Salindres in Gard, and at Gardanne, Le Rousset, La Barasse, and St. Louis les Aygualades in Bouches du Rhone. Considerable quantities, however, are exported and are refined in Great Britain, Germany, and the United States. The ports of shipment are San Raphael, Toulon, and Port de Bouc for Var bauxite and Cette for Herault bauxite.

French bauxite varies considerably in its physical and chemical characteristics. Some of it is hard, dense, and blocky, some is oolitic or pisolitic, and some of it is moderately soft and earthy. It is characteristically dark red and fairly high in iron oxide, but light-red, gray and cream-colored ore is found locally. The dark-red bauxite, as a rule, contains 20 to 25 per cent iron oxide while the light-colored varieties contain 4 to 12 per cent iron oxide. The light-colored bauxite ranges from 8 to 16 per cent in silica as compared with 2 to 5 per cent in the dark-red ore, while the alumina content in the light-colored ores ranges from 50 to 65 per cent and in the dark-red ores from 56 to 60 per cent. The combined water ranges from 11 to 14 per cent. The light- and dark-colored varieties may occur in the same deposit or they may be found in separate deposits.

United States.

Most of the United States bauxite production is from the Saline County and Pulaski County mines in Central Arkansas. Bauxite was discovered in Arkansas in 1890 but shipments did not begin until 1899. Since that time, the annual tonnage produced has gradually increased to a maximum of 562,892 tons in 1918. Since that date the output has been diminishing.

The bauxite mines of Georgia, Tennessee, and Alabama occur in groups, the most important of which are those along a belt extending from Irwinton (Wilkinson County, central Georgia) southwestward through Andersonville (Sumter County) and Springvale (Randolph County) to Clayton (Barbour County, southeastern Alabama.) Those in the Rome and Cave Springs districts (northwestern Georgia) and near Rock Run (northeastern Alabama), and those in the Chattanooga district (Tennessee) have also been of considerable importance. The Georgia-Tennessee-Alabama field has never been a large producer of bauxite but has had a steady annual production since 1889, when the first bauxite produced in the United States was shipped from Georgia. The maximum annual production was 62,134 tons in 1917. Bauxite was first found in the United States in 1883 near Rome, Georgia.

The United States bauxites differ from those of Europe in generally being white or gray, because of their relatively low iron oxide content, while those of Europe are commonly dark red and high in iron oxide. The average range in iron oxide in Arkansas bauxite is from 2 to 7 per cent, whereas the range of this constituent in Georgia, Tennessee and Alabama bauxite is from 0.5 to about 3 per cent. Exceptions occur in both fields, however, and the iron oxide may be as high as 12 or 14 per cent in particular deposits. The alumina content of the Arkansas bauxite is from 56 to 59 per cent, while the average range in silica is from 5 to 8 per cent. In Georgia, Tennessee, and Alabama the alumina content of the bauxite is from 54 to 58 per cent, and the silica from 7 to about 12 per cent.

Scattered occurrences of diasporic clay are found in association with deposits of flint clay in Maries, Osage, Gasconade, and neighboring counties in central Missouri. The flint clay is in pockets and the diasporic clay is in irregular masses included in the pockets. When the clay contains 70 per cent or more Al_2O_3, it is designated diasporic clay, and when it contains 50

to 70 per cent Al_2O_3, it is known as burley clay. Ordinary flint clay usually contains less than 50 per cent Al_2O_3. Small quantities of burley clay and diasporic clay have been mined recently in connection with flint clay and have been used for the manufacture of refractory products, chemicals, and abrasives.

Hungary.

Bauxite was discovered in western Hungary in 1921, near Halimba in the Bakony Forest, north of the western end of Lake Balaton. More recently, deposits have been discovered in the Vertes Mountains about half way between the Bakony Forest and Budapest, and the exploitation of these was started in 1925. The first important production of bauxite from western Hungary occurred in the Fall of 1926, and in 1927 shipments reached a total of over 280,000 tons. Practically all of the bauxite has come from the Gant region in the Vertes Mountains and has been exported to Germany.

The bauxite of western Hungary is yellow, brownish red, or mottled yellow and brown. It ranges from 57 to 62 per cent in Al_2O_3; 2 to 7 per cent in SiO_2; 12 to 20 per cent in Fe_2O_3; 2.50 to 3.50 per cent in TiO_2; and 14 to 16 per cent in combined water. The deposits now mined occur mostly with a thin overburden of soil or locally with a few feet of overlying limestone.

Dutch Guiana.

Bauxite was discovered in Dutch Guiana early in 1915, but no shipments were made until 1922. Shipments have consistently increased until 1928, when a total of 203,459 tons was shipped. Most of the bauxite is exported to the United States and Canada for the manufacture of aluminum. It has the following average composition: Al_2O_3, 59.00 per cent; SiO_2, 2.00 per cent; Fe_2O_3, 6.50 per cent; TiO_2, 2.50 per cent; combined water, 30.00 per cent.

The principal deposits occur in several groups along the Suriname, Cottica, and Coermotibo Rivers from about 15 to 100 miles from the coast. They are in the form of knolls and small hills rising above the low, swampy coastal plain region. A few deposits located farther inland occur as lateritic cappings of plateaux and of isolated flat-topped hills that form part of the interior highlands.

British Guiana.

Bauxite was discovered in British Guiana in 1910; exploitation started in 1915 and the first shipments were made in 1917. In 1928 the shipments amounted to 165,422 tons. The deposits occur in the coastal plain region about 60 to 80 miles inland and are similar, in general, to the deposits of Dutch Guiana. They occur in several groups near the Demerara and Berbice Rivers, and, as in Dutch Guiana, they are found as small hills rising above the general elevation of the coastal plain. Some have a considerable thickness of loose, sandy and clayey sedimentary overburden.
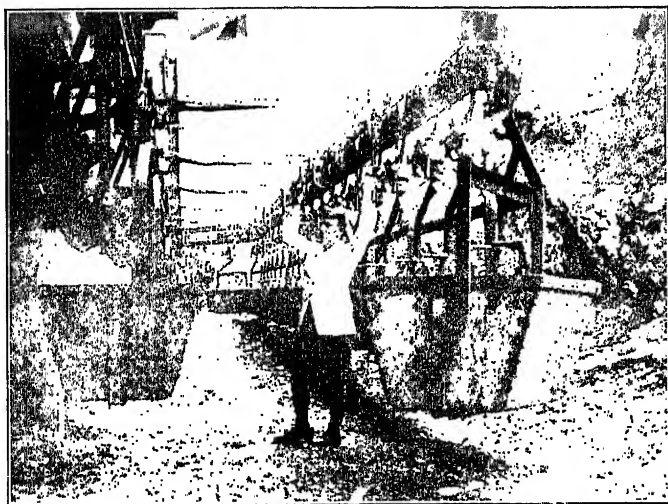
FIG. 27. Loading buckets at cableway loading station for transportation to coast, Istria.

Most of the British Guiana bauxite is shipped to Canada and the United States for use in the chemical industries and for the manufacture of aluminum. It has the following average composition: Al_2O_3, 61.00 per cent; SiO_2, 2.75 per cent; Fe_2O_3, 2.50 per cent; TiO_2, 2.75 per cent; combined water, 31.00 per cent.

Yugoslavia.

Bauxite deposits occur in many parts of Yugoslavia, but most of those now (1929) being mined are in Dalmatia near the Adriatic coast or on some of the small neighboring islands. Large undeveloped deposits, however, occur in the interior of

Croatia and Herzegovina and along the coast in Montenegro.
A small occurrence of bauxite (wocheinite) is reported from the
district between Feistritz and Lake Wochein, Carniola.   The
more important deposits in Yugoslavia are those in the Obrovac
and Drnis districts of Dalmatia, in the Kotor and Bar regions
of Montenegro, and in the Mostar region of Herzegovina.

The bauxite occurs as layers, lenses and pockets in limestone,
usually outcropping at the surface with little or no soil over-
burden; many extend to considerable depths.   Most of the
bauxite is dark red and high in iron, but some pink and cream-
colored bauxite moderately low in iron occurs.   In general,
the dark-red bauxite contains 48.00 to 54.00 per cent Al_2O_3;
1.00 to 4.00 per cent SiO_2; 20.00 to 24.00 per cent Fe_2O_3; 2.50
to 3.50 per cent TiO_2, and 18.00 to 24.00 per cent combined
water.   This great range in composition is mainly due to the
fact that the ores vary in character in different districts.   Bauxite
from a single source generally has a fairly uniform composition.

The bauxite mined in Yugoslavia has been used mainly in
Europe, but recently a considerable tonnage has been shipped
to the United States for the manufacture of aluminum and high
alumina cement.

Italy.

Bauxite occurs in Italy in two main districts: (1) the Istrian
Peninsula and (2) the central Apennine Mountain region.   The
deposits of Istria are similar to those of Yugoslavia, being in
the form of numerous pockets and lenses enclosed in limestone.
These pockets are more or less segregated into groups, of which
the most important are in the vicinity of Buje, Visinada, Pisino,
Gimino, San Domenica, Albona, and Barbana in the central
part of the peninsula, and near Lavarigo, Altura, and Sissano
in the southern part.   The mining of bauxite in Istria on a large
scale began during the World War and the maximum production
was reached in 1925, when a total of 181,586 long tons was
produced.   Most of the Istrian bauxite has been exported to
Germany for use in the manufacture of alumina and chemicals.

Istrian bauxite is of two main types: (1) dark-red ore similar
to that of Dalmatia and (2) light-colored variegated ore.   The
former generally averages between 54 and 58 per cent Al_2O_3;
22 and 26 per cent Fe_2O_3; 2 and 4 per cent SiO_2; 2 and 3 per cent
TiO_2; and 12 and 15 per cent combined water.   The latter

mmonly carries 60 to 66 per cent Al_2O_3; 5 to 9 per cent SiO_2; 10
16 per cent Fe_2O_3; 3 to 5 per cent TiO_2; and 12 to 15 per cent
mbined water. In many deposits, the light-colored, varie-
ted bauxite occurs as an enclosing layer, while the dark-red
uxite forms the central core. Elsewhere, however, the two
pes may occur more or less intermixed in the same deposit
they may be found in separate deposits.

The bauxite in the central Apennines region occurs in two
oups, one in the province of Aquila, about 50 miles east of
ome, and the other in the province of Benevento, about 30
iles north of Naples. Bauxite from these deposits has been
ined mainly for the local manufacture of abrasives and chemi-
ls. Some of the deposits are noted for their high iron content
eraging between 25 per cent and 30 per cent Fe_2O_3. The
nual production has generally been less than 15,000 tons.

reece.

Bauxite deposits have in recent years been discovered in Greece
the Distomon district north of the Gulf of Corinth. The ore
curs as layers and pockets in limestone and known deposits
cur over an area of about 100 square kilometers bordering the
ulf of Corinth. A few shipments have been made which show
e ore to have approximately the following composition: Al_2O_3,
to 59 per cent; SiO_2, 3 to 7 per cent; Fe_2O_3, 16 to 21 per cent;
O_2, 2 to 2.50 per cent; combined water, 13 to 16 per cent.

dia.

Bauxite occurs in many parts of India, but principally in the
lgaum, Kolhapur, and Ratnagiri districts (south of Bombay),
the region north of Bhopal (Central India), in the Jubbulpore
d Balaghat districts (Central Provinces), in the Ranchi district
ihar and Orissa), in the region north of Vizagapatam (Madras),
d in the Jammu district (Kashmir). Bauxite has been mined
Khaira, north of Bombay, and elsewhere in small quantities,
ostly for local chemical use and for petroleum filtration.
igh freight rates and competition from European bauxite have
evented extensive exportation. The Indian bauxite in the
stricts that give commercial promise contains about 56 to 62
r cent Al_2O_3; 1 to 4 per cent SiO_2; 3 to 10 per cent Fe_2O_3; 3
10 per cent TiO_2, and 25 to 28 per cent combined water. The
mmu bauxite is diasporic in character and carries about 60 to

70 per cent Al_2O_3; 12 to 20 per cent SiO_2; 0.5 to 2 per cent Fe_2O_3; 2 to 4 per cent TiO_2, and 11 to 13 per cent combined water.

Ireland.

A small quantity of bauxite has been mined annually for many years in County Antrim, northeastern Ireland, most of it being used locally.   The Irish bauxite is of low grade, containing a high percentage of iron oxide, silica, and other impurities.   It occurs in layers and lenses associated with iron ore and lithomarge in a bed underlain and overlain by basalt flows.
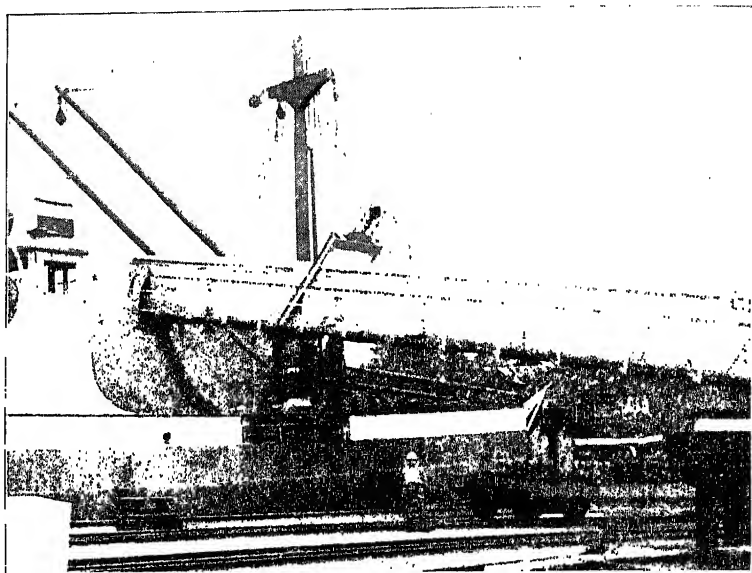
Fig. 28.—Showing method of loading ocean-going steamers; Dutch Guiana.

Rumania.

Important deposits of bauxite occur in the Bihar Mountains, western Rumania.   The main deposits are in the Poiena, Sebes Körös and Jada valleys tributary to the railroad between Nagy-varad (Grosswardein) and Koloszvar (Klausenburg), and in the Galbina Valley southeast of Belenyes.   These deposits were operated during the World War to supply the aluminum require-ments of the Central Powers, but no information is available as to tonnage produced.   The production has been small since the World War, as the deposits are far from the market and the

ε is not very desirable industrially, because of its refractory aracter. Most of the bauxite is dark red or brown and high iron, but gray bauxite low in iron and high in silica occurs ally. The red ore has the following average composition: $_2O_3$, 55 to 65 per cent; Fe_2O_3, 20 to 30 per cent; SiO_2, 2 to 6 r cent; TiO_2, 3 to 4 per cent; loss on ignition 10 to 13 per cent.

stralia.

In Victoria, Australia, small quantities of bauxite have been oduced annually in recent years in the Gippsland district, rth of Melbourne, mostly for use in the manufacture of uminum sulphate at Melbourne.

The extensive laterite deposits of western Australia and of w South Wales are as yet undeveloped.

rmany.

During the World War small deposits of impure bauxite were ned in the Vogelsberg Mountains east of Giessen, Hesse-rmstadt. These deposits are a residual weathering product erlying basalt, most of the bauxite being found as nodules in y. Since the war these mines have been operated only inter-ttently because high-grade ores have become available from ance, the Adriatic district, and from western Hungary.

ain.

Scattered deposits of bauxite occur in the provinces of Barce-a and Tarragona, northeastern Spain; the main occurrences near Mediona, La Llacuna, and Poblas. They consist of ckets in limestone. Some high-grade ore is found, but much the material in the pockets is uncommercial. A small amount ore has been mined, but at present the mines are idle.

MINING AND MILLING OF BAUXITE

As already explained, bauxite varies greatly in composition l in content and character of impurities. This is true both hin individual deposits and as between different deposits and ferent districts. Moreover, the shape of deposits and their ations to the enclosing rocks, as well as the character of the losing rocks, vary in different localities. For these reasons, methods of mining bauxite differ considerably in different ces.

In general, the operations that bauxite undergoes in its passage
from the mine to the manufacturing plant (which may be in
the nature of a concentrating plant where alumina and aluminum
hydrate are produced, a chemical plant where aluminum sulphate
or other aluminum compounds are produced, an electric furnace
plant where artificial abrasives are produced, kilns or furnaces in
which alumina cement is produced, or ovens in which refractory
products are made) may include stripping, mining, crushing,
washing, drying, pulverizing, and calcining. Not all or even
most of the bauxite produced passes through all of these processes
In fact, most of the processes, such as washing, drying, pul-
verizing, and calcining, are used only in a few localities.

Stripping.

When bauxite occurs under an overburden of unconsolidated
material of moderate thickness, this is usually removed and the
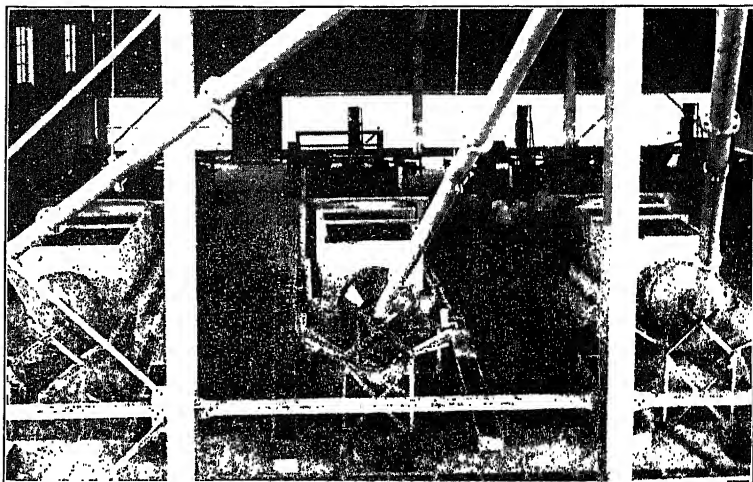
Fig. 29.—Washing bauxite; Dutch Guiana.

bauxite is mined in open pits. The overburden may consist of
either a thin layer of soil or unconsolidated beds of sand and clay.
The maximum depth that can be economically stripped depends
upon a number of factors, among which are the thickness of the
bauxite bed, the character of the overburden, and the cost of
disposing of it. In some places as much as 40 or 50 feet of over-
burden have been removed.

Where the overburden is thin, it is generally removed by hand and the surface of the ore is cleaned in the same operation. Where the overburden is of moderate thickness, it may be more economical to remove the bulk of it by means of steam shovels or other stripping apparatus, after which stripping by scrapers and by hand and cleaning of the ore surface are necessary before mining operations can commence. Stripping with steam shovels is practically confined to the bauxite mines of North and South America, this operation being carried out in European bauxite mines by hand, with or without the use of scrapers.

Mining.

Bauxite is usually mined by open-pit methods, but there are some localities where underground mining is necessary on account of the great depths of overburden or the character and attitude of the bauxite deposits. In open pit mining the bauxite beds are generally worked in vertical or nearly vertical faces. Where the thickness of the bauxite bed or pocket is moderate, the ore is mined in one bench. In a few places, however, where the bauxite masses are of considerable thickness, two benches, and occasionally three benches are used. Bauxite is generally moderately hard and compact and, therefore, explosives are used to shatter the ore. After the ore is broken down, it may be loaded by steam shovel or by hand.

In places where the floor of the open pits is approximately on the same level with or only slightly below the surrounding region, the bauxite is loaded into mine cars of small capacity and hauled by means of mules or small locomotives to loading bins or milling plants. During the mining and loading into mine cars, when this is done by hand, there is generally a separation made of clay and low-grade bauxite from the commercial bauxite. In open-pit mines where the floor of the mine is sunk beneath the surrounding surface, the bauxite is loaded into mine cars or into buckets and hauled to the surface by means of inclined railways or vertical hoists.

Underground mining is employed on horizontal bauxite beds when the overburden is too thick to be economically removed by stripping, or on steeply dipping beds underlain and overlain by moderately hard, compact rocks. In the case of horizontal beds, the underground mining is by means of drifts and stopes;

whereas, in the case of steeply dipping bauxite beds, mining is by means of inclines and drifts.

At the European mines the bauxite is generally shipped in the condition in which it leaves the mine; that is, there is no further treatment of the ore until it reaches the consuming plant, where it is subjected to whatever further treatment is required for consumption in that particular industry. In the North and South American mines, however, most of the bauxite after it is mined is transported to milling plants, where it undergoes further
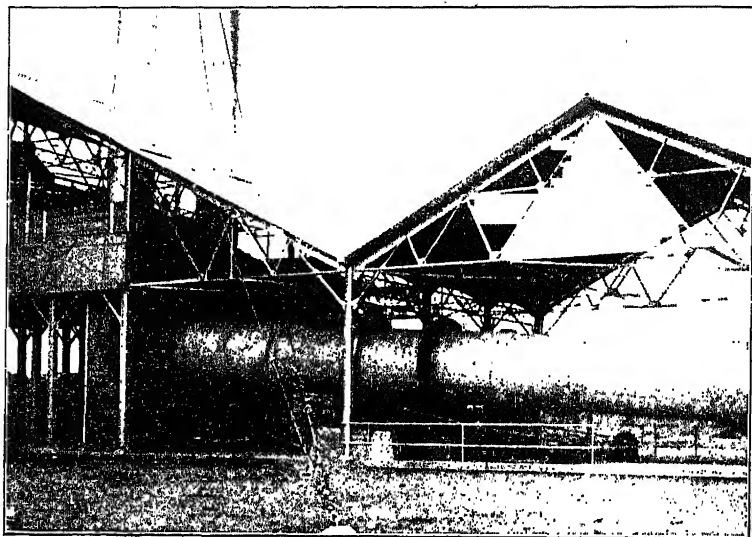
Fig. 30.—Drying bauxite in rotary kilns; Dutch Guiana.

treatment, such as crushing, washing, and drying, before it is shipped to the consuming industries.

Crushing.

Bauxite is commonly crushed in gyratory or jaw crushers, the maximum size produced varying from 1 to $3\frac{1}{2}$ inches. The proportion of the coarse to the fine material varies according to the hardness and toughness of the bauxite.

Washing.

After crushing, the ore may go directly to drying kilns or it may be subjected to preliminary washing in order to remove

clay and other light impurities. Washing formerly was done by means of log washers, but in recent years special combination trommel and rake washers have been designed and have been found to be very satisfactory.

Drying.

Bauxite as mined may contain from 6 to 20 per cent free moisture. The European bauxite differs from the North American and South American bauxite as mined in usually having a moisture content of less than 10 or 12 per cent, whereas American bauxite generally has more than 10 per cent moisture. The free moisture is removed by passing the bauxite through cylindrical drying kilns, which range in length from 40 to 120 feet and in diameter from 3 to 8 feet, according to the capacity required and the maximum moisture content allowed in the final product. This varies from 1 to 5 per cent. Such cylindrical kilns are fired by means of wood, coal, oil, or gas. Pulverized coal has been found to be very satisfactory. Small and short kilns are less efficient than long kilns.

Pulverizing.

Most industries that consume bauxite require it in the pulverized form, usually of a fineness of 80 or 100 mesh. This pulverizing is generally done where the bauxite is consumed, but some small works prefer to purchase bauxite in pulverized form. A few bauxite mills, therefore, have equipment for grinding bauxite to 80 or 100 mesh size.

Calcining.

As already stated, commercial bauxite contains from 14 to more than 30 per cent of combined water. This combined water is not removed by ordinary drying but requires much greater heat than is attained in the drying kilns. Certain industries, such as the artificial abrasives industry, require bauxite from which the combined water as well as the free moisture is removed. This is done by means of calcining kilns, which are much like drying kilns, except that the refractory linings are heavier and the rotation and feed are slower. They are usually so operated that the bauxite when it leaves the kiln has a temperature of approximately 1700 to 1800°F., whereas the bauxite when it leaves the ordinary drying kilns has a temperature of about 200 to 250°F. After passing through calcining kilns, the bauxite contains no

moisture, and generally less than 1 or 2 per cent combined water. The alumina content may range from 70 to 85 per cent or even higher, depending upon the amount of impurities present.

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CHAPTER V

THE PRODUCTION OF ALUMINA

By

Junius D. Edwards and Ralph B. Mason

Aluminum is the most widely distributed of the metals, and material containing 10 to 35 per cent aluminum oxide can be found in great abundance the world around. It is not economical to extract aluminum from these lean ores, however, while bauxite carrying 50 to 60 per cent of alumina is generally available. A similar, but more familiar, situation exists in the case of iron, which is as widely distributed as aluminum and in almost as great abundance. Immense deposits of rocks, clays, and the like containing 10 per cent and more of iron can be found almost anywhere, but no one thinks of using such poor material for the production of iron while there is still available a supply of the rich hematite, limonite, and magnetite ores carrying 50 to 60 per cent iron. Nevertheless, hosts of inventors have worked on processes for the extraction of alumina from clay, feldspar, alunite, and other aluminous materials without any commercial result. While it is possible to extract and purify the alumina from clay, yet the cost of chemicals, energy, and labor makes the procedure impractical from a commercial standpoint at present.

One important difficulty in alumina production arises from the fact that the analogy between iron and aluminum ceases when the reduction process is reached. Iron is an easy metal to reduce from its oxide. The ore only needs to be charged into the blast furnace with limestone and coke and the furnace blown with air. The reducing gases from the coke convert the iron to the metallic form, and the impurities, such as silica and alumina, pass into the slag. Alumina, on the contrary, is a very difficult oxide to reduce, and when it is converted into aluminum (*e.g.*, by electrolysis) most of the associated impurities are likewise reduced to form metals or metalloids which alloy with and contaminate the metal. The ore of aluminum must,

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therefore, first be treated so as to eliminate substantially all
of the impurities. Purified alumina suitable for the production of
aluminum usually contains a total of less than 0.1 per cent
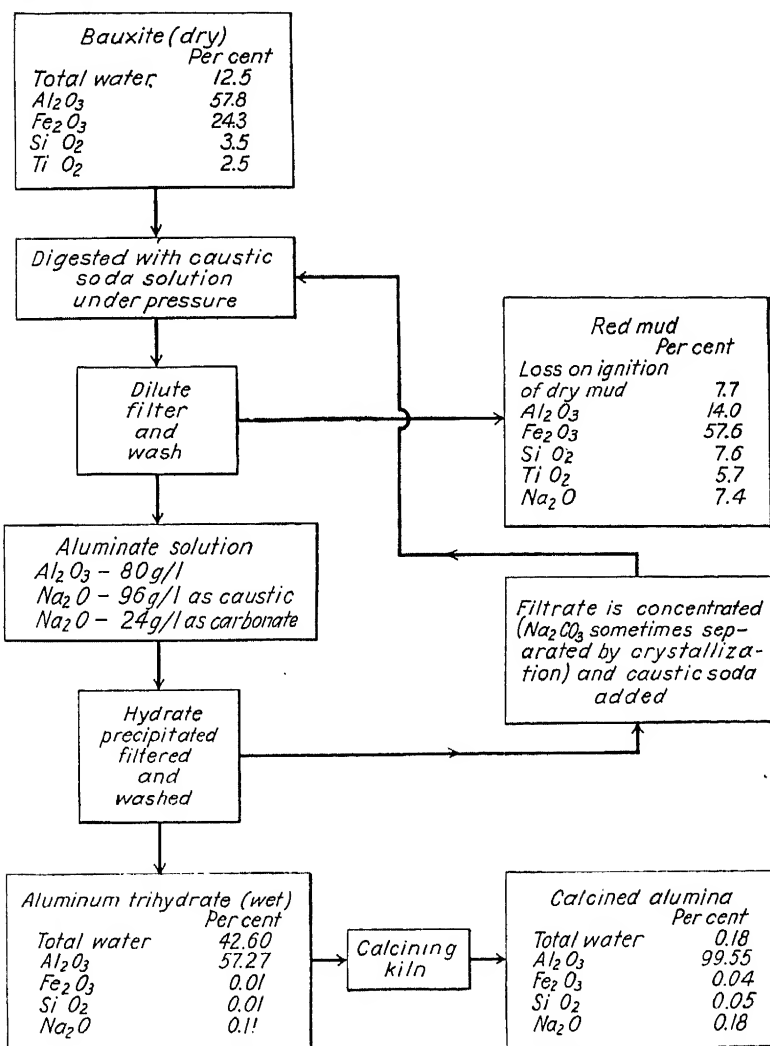
FIG. 31.—Diagram of Bayer process for producing alumina (bauxite ore concentrates).

of the oxides of iron, silicon and titanium, and is a highly refined
or concentrated product. The purification is a relatively expen-
sive process, and as it takes about two pounds of alumina (1.89 is

the theoretical requirement) to produce a pound of aluminum, the cost of the alumina is an appreciable item in the cost of aluminum. This is the reason for the great interest displayed in processes of producing pure alumina.

In the commercial production of alumina from bauxite, the general practice is to convert the alumina by reaction with alkali into sodium aluminate, which is readily soluble in water. The sodium aluminate solution is then filtered off and the residue containing the iron, silicon, and titanium of the bauxite is thrown away. The solution containing the alumina is treated so as to precipitate pure aluminum hydrate, which is separated, and the alkali in the solution is returned to the process. The aluminum hydrate is washed and finally heated to a high temperature to drive off all the water and convert it into pure dry aluminum oxide, Al_2O_3, which is ready to be used in the production of aluminum.

There are two general procedures employed to produce the sodium aluminate solution. In the Bayer process, which is the one most widely used, the bauxite is digested under pressure with hot sodium hydroxide to form a solution of sodium aluminate. The alternative procedure is to heat the bauxite with sodium carbonate in a furnace or rotary kiln to form solid sodium aluminate. The sodium aluminate can then be leached out and the alumina recovered from the solution.

Aluminum hydrate can be precipitated from the aluminate solution by neutralizing with carbon dioxide. This was the original method used in commercial production. At present the more common procedure, particularly in the Bayer process, is to cool and agitate the solution in the presence of a "seed" charge of aluminum hydrate, whereupon about two-thirds of the dissolved hydrate slowly crystallizes out.

Bayer Process.

The Bayer process is today the most widely used method for the production of alumina. A detailed description of this fundamental process will therefore be given before proceeding to the consideration of other methods of recovering pure alumina from its ores.

The major portion of the aluminum oxide in bauxite dissolves when it is heated with a solution of sodium hydroxide (caustic soda), but it is not attacked by a solution of sodium carbonate.

There is good reason for believing that the alumina, by reaction with the caustic soda, is converted into soluble sodium aluminate, to which is ascribed the formula $NaAlO_2$. The iron oxide of the bauxite is insoluble in the sodium hydroxide solution and aside from increasing the bulk of the insoluble residue, which must be filtered and thrown away, has little effect on the process. The silica content of the bauxite is, however, very important, since it is the cause of serious losses of both soda and alumina. During the digestion there is apparently formed an insoluble sodium aluminum silicate which carries both soda and alumina into the "red mud," as the bauxite residue is called. Karl Josef Bayer[1] has ascribed the formula, $Al_2O_3.Na_2O.3SiO_2.9H_2O$, to this compound. Whether it actually has this composition or some other has not been definitely ascertained. Certain it is, however, that, with increasing content of silica in the bauxite, both soda and alumina losses increase. Experience indicates that for every pound of silica in the bauxite, 1.1 to 2 pounds of alumina, and 1 to 3 pounds of soda (calculated as sodium carbonate) are lost. The soda loss appears to vary considerably, depending on the character of the bauxite which is being digested and the conditions of digestion. It is quite essential, therefore, in selecting ore for the Bayer process to limit the silica to as low a figure as circumstances warrant. In America, bauxites are used which carry as high as 7 per cent silica; while in Europe, where a relatively large supply of low-silica bauxite is available, the bauxites employed usually contain less than 5 per cent silica. In selling bauxite to the aluminum industry, it is commercial practice to charge the producer a penalty for each unit of silica in excess of some stated amount, such as 3 per cent. Titanium oxide is also said to combine with soda to form insoluble sodium titanates and still further increase the soda losses. In view, however, of the refractory character of most titanium minerals, there is some question as to the extent of such a reaction.

Preparatory to the digestion process, the bauxite is dried and ground. The drying is necessary in order to permit the grinding of the material to a fine powder. Fine grinding (80 to 100 mesh) is essential in order to secure efficient extraction

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[1] BAYER, KARL JOSEF, U. S. Pat. 515,895, Mar. 6, 1894; Ger. Pats. 43,977, Aug. 3, 1888; 65,604, Nov. 3, 1892. For constitution of red mud, see also B. WAESER, *Metallbörse*, **13**, 2075 (1923).

of the alumina. The drying ordinarily employed merely removes the free water of the bauxite but leaves the combined water, or water of hydration. Ullmann,[1] however, states that it has been the practice at some plants to calcine the bauxite at temperatures of 350 to 400°C. before grinding. This calcination is said to have a beneficial effect in destroying organic matter, such as humus acids, which dissolve and accumulate in the alkali
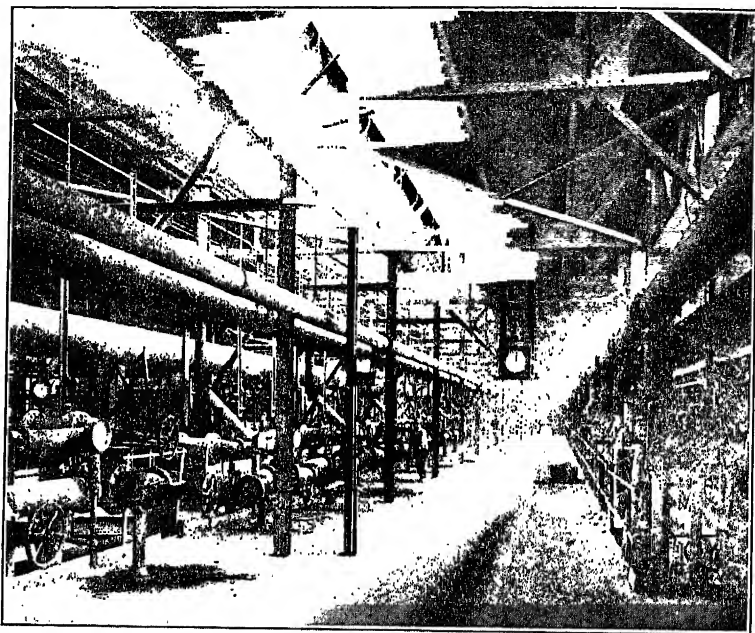
FIG. 32.—Digester room in alumina works.

solutions used for digestion.[2] It may have the disadvantage, however, of rendering the alumina less readily dissolved.[3] The trihydrates begin to lose their combined water at relatively low temperatures, 150 to 250°C., while the monohydrate bauxites can be heated to substantially higher temperatures, 400 to 500°C., before the loss of water becomes rapid.

In the digestion of bauxite with sodium hydroxide, the ideal aimed at is to dissolve as much as possible of the contained alumina in the shortest possible time and, simultaneously, to

[1] ULLMANN, "Enzyklopädie der technischen Chemie," **1**, p. 312.

[2] HALL, C. M., U. S. Pat. 663,167, Dec. 4, 1900; Br. Pat. 14,573 of 1900; Ger. Pat. 138,219, Jan. 3, 1903.

[3] PHILLIPS, W. B., J. HANCOCK, *J. Am. Chem. Soc.*, **20**, 209 (1898).

produce a solution from which a maximum amount of alumina can be precipitated per unit of volume. Increasing the temperature of the solution and the concentration of sodium hydroxide increases the amount of alumina which can be dissolved. The more concentrated the alkali solution, however, the more alumina it will retain at the end of the precipitation cycle, and the greater the difficulties experienced in its filtration. Filtration is usually carried out in presses using heavy cotton
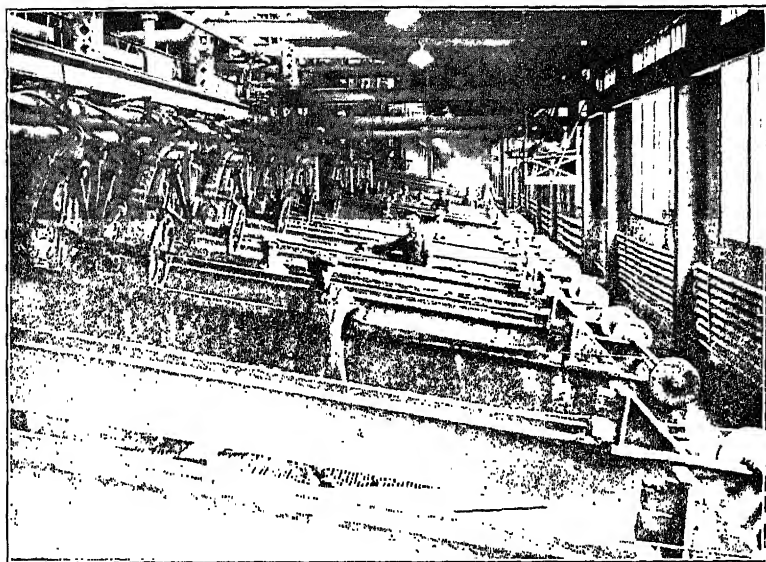
Fig. 33. Filter presses for red mud; press in rear is open showing filter leaves.

cloth over steel frames, and the filter cloth shows excessive deterioration when the hot alkali is too concentrated. Under such conditions, it is customary to dilute the solution before filtration. All of these factors require a nice balance in an efficient process. Bayer recommended digesting at 160 to 170°C. for a period of $1\frac{1}{2}$ to 2 hours. An excess of soda over the 1:1 ratio Al_2O_3/Na_2O is required in order to hold the alumina in solution during the filtration. Bayer recommends that the molecular ratio of Al_2O_3 to Na_2O in the aluminate solution should be about 0.55 (1:1.8). In a recent British patent to Finkelstein,[1] the original Bayer procedure using solutions above

[1] FINKELSTEIN, A., Br. Pat. 248,746, July 4, 1927.

1.4 in specific gravity has been modified and a solution of sodium hydroxide of specific gravity not greater than 1.36 is used to digest the bauxite at 170°C. The use of weaker solutions of sodium hydroxide for certain bauxites was, however, common practice long before Finkelstein's patent. The digestion is carried out in steel digesters, heated by steam under pressure, and provided with some device for stirring or agitating the charge. When digestion is complete, the charge is pumped to filter presses where the hot aluminate liquid is separated from the residual "red mud." The filter cake is washed and the first portions of the wash water are added to the concentrated aluminate solution.

The aluminate solution is then pumped to the precipitating tanks where it is mixed with a "seed" charge of aluminum hydrate from a previous cycle. The mixture must be continually agitated and gradually cooled under conditions which permit the formation of coarsely crystalline aluminum trihydrate. Ullmann states that the most favorable range of temperatures for precipitation lies between 25° and 35°C. The amount and particle size of the seed charge added, the rate of cooling, degree of agitation, etc., should be such as to minimize the production of extremely fine and powdery crystals of aluminum hydrate which would be difficult to calcine without excessive dust loss, and which would later cause excessive loss by dusting when the alumina is thrown on the electrolytic cells. Bayer states that the molecular ratio of alumina to soda (Al_2O_3/Na_2O) should be as low as 1:6 at the end of the precipitation cycle. The precipitated alumina is finally filtered off or otherwise separated[1] from the solution, washed, and sent to the calciners. There the hydrate is heated in rotary kilns to a temperature substantially above 1000°C. in order to convert it into anhydrous and non-hygroscopic alumina suitable for use in the electrolytic reduction process. The addition of a small amount of hydrofluoric acid or aluminum fluoride[2] to the hydrate makes the dehydration more complete and decreases the temperature of calcination. The solution contains appreciable quantities of alumina and the soda; it is concentrated by evaporation, and,

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[1] *e.g.*, by continuous settling. SHERWIN, R. S., U. S. Pat. 1,314,709, 1,314,710, Sept. 2, 1919.

[2] PÉCHINEY, A. R., U. S. Pat. 811,433, Jan. 30, 1906. CIE DES PRODUITS CHIMIQUES D'ALAIS ET DE LA CAMARGUE, Fr. Pat. 349,709, June 9, 1905; 1st Add. 7224, June 13, 1907; Ger. Pat. 165,612, Nov. 20, 1905.

after the addition of more sodium hydroxide to bring it up to the required strength, it is used for the digestion of a new charge of bauxite. Some sodium carbonate may crystallize out of the liquor during evaporation if the concentration is high.

In Fig. 31 is shown a diagram illustrating the main steps of the Bayer process as practiced at one plant. This diagram includes typical analyses giving the composition of the raw materials and products at various steps in the process. With other types of bauxite and other operating conditions, as well
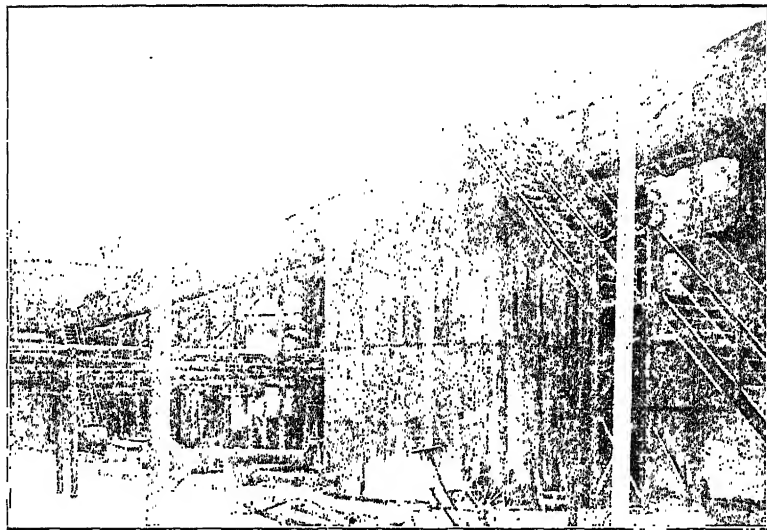
FIG. 34.—Concentrating and washing aluminum hydrate.

as with normal variations at this plant, substantial differences in the composition of the various materials will be observed. For the purpose of illustration, however, these data may be taken as typical.

Furnace Process of Producing Sodium Aluminate.

The furnace process of producing sodium aluminate from bauxite by heating with sodium carbonate has already been referred to. The process, sometimes called the "Deville-Péchiney process," was early investigated by Le Chatelier and Morin (1858 to 1863) and has since been developed by many others. The reaction may be represented as follows:

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2.$$
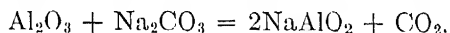
The finely ground bauxite is uniformly mixed with powdered soda ash (Na_2CO_3) and the charge thus prepared is sintered by heating to the reaction temperature. Fused sodium carbonate not only reacts with alumina to form sodium aluminate, but also with ferric oxide to form sodium ferrite, with titanium oxide to form sodium titanate, and with silica to form sodium silicate. In the subsequent leaching process, the sodium ferrite reacts with water to form insoluble ferric hydroxide and sodium hydroxide, while the silica is mostly precipitated as sodium aluminum silicate. The sodium aluminum silicate and
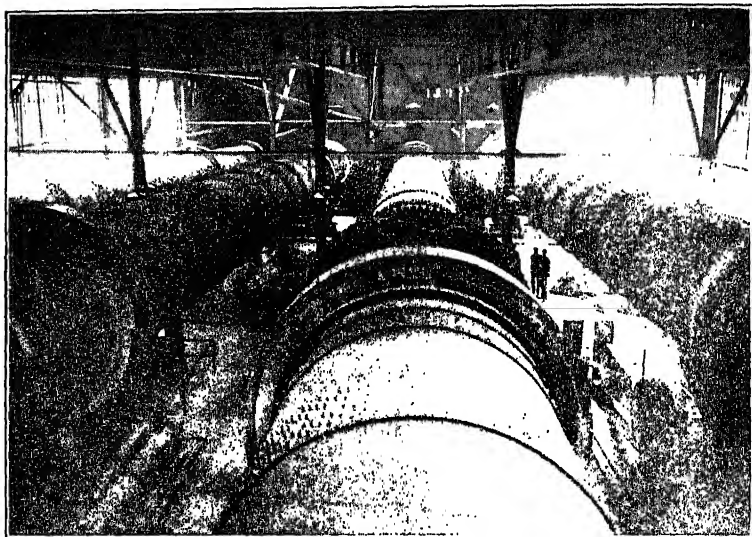
Fig. 35.— Calcining kilns for alumina; view from feed end.

sodium titanate formed represent real soda losses, and, in addition, the silica may contaminate the product. Lime is sometimes added to react with the silica and form insoluble calcium silicate. Low silica bauxites are obviously desirable for this process, as well as for the Bayer process. It is necessary to use more than 1 mol of sodium carbonate for each mol of alumina in order to force the reaction to completion.

The heating of the charge was formerly carried out in reverberatory furnaces, but modern practice employs the rotary kiln. In order to secure complete reaction between the soda and alumina, the temperature is usually carried substantially above 1000°C. Gunther Feld states that the reaction between sodium
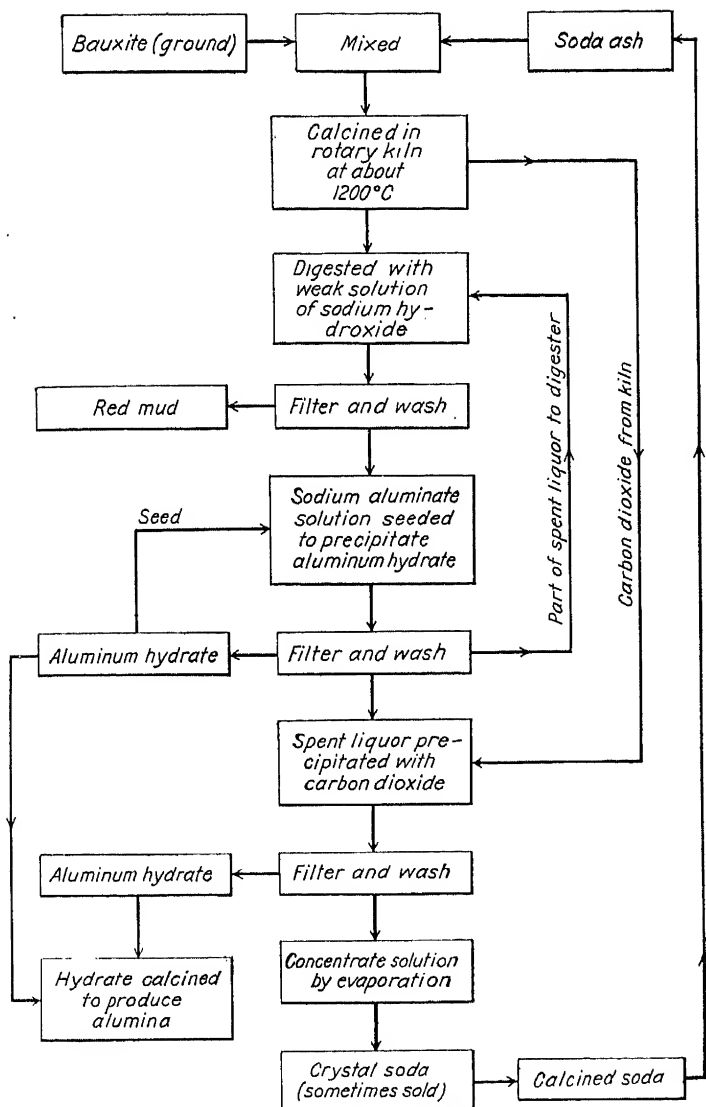
Fig. 36.—Diagram of furnace process for producing sodium aluminate and alumina.

carbonate and the alumina of bauxite is complete at 950°C. with the formation of $NaAlO_2$.[1] J. W. Cobb, experimenting with pure ignited alumina, found that the reaction of Na_2CO_3 with Al_2O_3 in equimolecular proportions began at 710 to 720°C., was extensive at 800°C., and complete at 1150°C.[2] Above 1150°C., the aluminate appeared to dissociate with the formation of alumina insoluble in N hydrochloric acid and with the volatilization of part of the soda. The product of the reaction is a crumbly mass which readily can be powdered and is quite hygroscopic.

It is promptly subjected to digestion with a weak solution of caustic alkali from a previous cycle of the process. The mixture of the aluminate and the alkali solution is heated to about 80°C. and agitated until maximum solution of the soluble alumina has been effected; the red mud is then filtered off. Although the molecular ratio of alumina (plus iron oxide) to soda in the fused aluminate is about 1:1.2, the ratio of alumina to soda in the solution, after digestion, should be about 1:1.8 in order to permit the proper extraction of the alumina. The clear solution of aluminate is now ready for recovery of the alumina. One method of precipitating the alumina is to saturate the solution with carbon dioxide, while the solution is held at a temperature of about 50 to 90°C. If the temperature falls too low, the hydrate precipitates in a form which is difficult to filter and carries down more of the soda and dissolved impurities. Another variation is to precipitate a substantial part of the alumina by the Bayer method employing a seed charge of hydrate, filter off the hydrate obtained in this way, and then (in the portion of the solution not required for leaching more aluminate) complete the precipitation of the alumina by saturating the solution with carbon dioxide. In either case, the solution is freed from alumina and concentrated by evaporation to recover the sodium carbonate as crystal soda. This sodium carbonate is then sold as such, or calcined for use again in the process.

OTHER PROCESSES FOR EXTRACTION OF ALUMINA

So many chemical processes for the extraction of alumina are being continually brought forward that a summary of the "prior art" will be useful to those interested in this field.

[1] FELD, G., *Z. angew. Chem.*, **39**, 174 (1926).

[2] COBB, J. W., *J. Soc. Chem. Ind.*, **29**, 399 (1910).

The Bayer process, as originally described by Bayer, is in ase today without many fundamental changes. Of course, there have been marked advances in the equipment employed 'or carrying out the process and each manufacturer has determined the conditions of digestion best adapted to his own bauxite supply. Many experimenters have worked on the improvement of the Bayer process, and it is of interest to examine the proposals which have been made. Some of these are fantastic and impractical under all conditions, some have a limited application, and others may be in use in one plant or another.

The alumina processes may be broadly divided into two classes: alkaline and acid. The practical processes above described are typical alkaline processes and show the characteristic advantages and disadvantages of their class. Briefly, we may say that iron causes no trouble in alkaline processes, ferric oxide being substantially insoluble in alkali solutions (except sulfides). Iron is thus easily and cheaply eliminated in the red mud, and practically all of the small amount of iron oxide in the precipitated aluminum hydrate is due to mechanical contamination (incomplete removal of the red mud in filtration, rust from pipes and tanks, etc.) and not to the chemical process. Silica, on the other hand, is always attacked by the alkaline processes and its elimination is often troublesome, usually more or less incomplete, and involves a loss of alkali and generally also a loss of alumina. Consequently, alkaline processes require a bauxite low in silica, while iron and titanium oxides are merely inert diluents, except for processes involving fusion or fritting with alkali. In these, iron oxide is advantageous because of its ability to causticize some soda, but titanium oxide may cause some loss of alkali.

Acid processes, on the contrary, always dissolve more or less of the iron, but most of them do not dissolve the silica. Titanium is likely to be partly dissolved. Any gelatinous or colloidal silicic acid formed by acid attack on the clay can be readily and quite completely removed, but the iron salts are so closely related to the aluminum salts in their chemical behavior that a complete separation is practically always difficult and expensive, and in most cases commercially impossible. From their nature, therefore, the acid processes are best adapted to the treatment of ores low in iron, such as kaolin, feldspar, alunite, leucite, or the relatively rare deposits of white bauxite. The
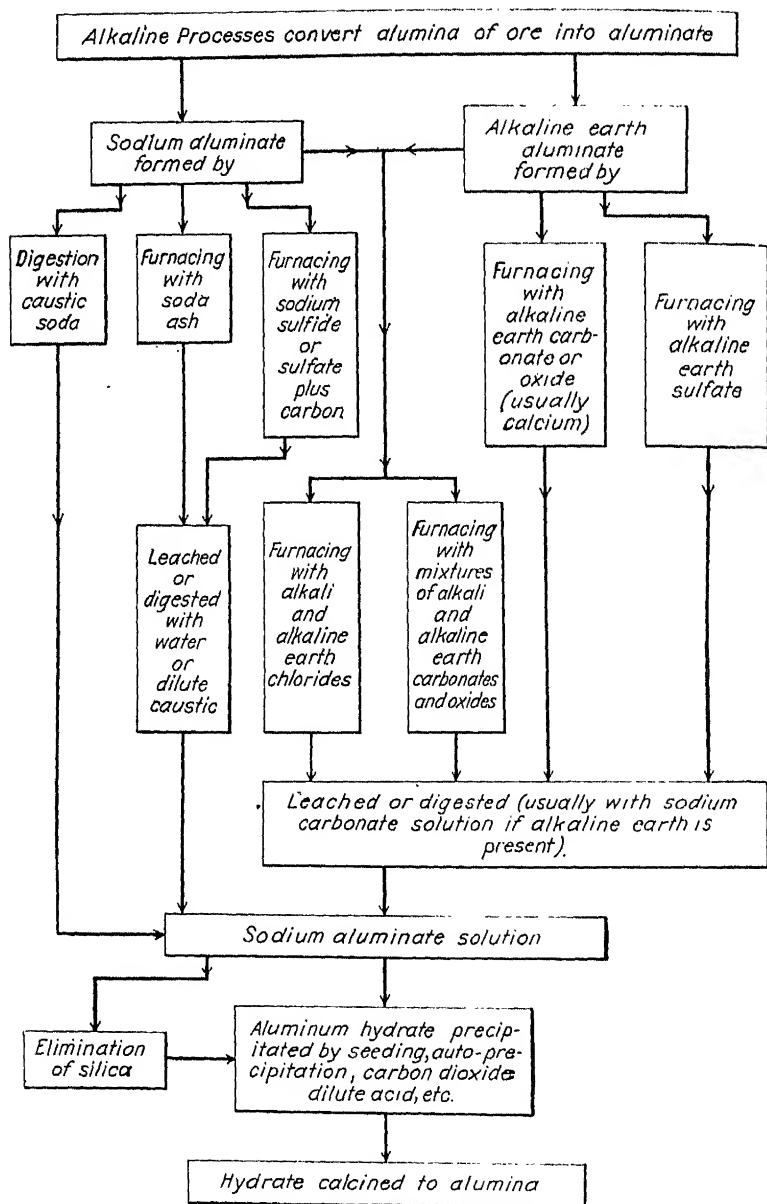
Fig. 37.—Outline of unit operations in alkaline processes for producing alumina.

relatively low alumina content of these ores (except the white bauxite), however, puts these processes under a serious economic handicap.

Because of their greater practical importance and the fact that the most important ones have already been outlined, the alkaline processes will be first discussed.

Miscellaneous Alkali Digestion Processes.

Bauxite is the only ore commercially treated by digestion with alkali hydroxide but patents have been issued on a variety of similar processes applied to other ores. For example, Piva[1] claims to be able to digest pulverized leucite with concentrated potassium or sodium hydroxide under a pressure of 20 to 25 atmospheres and obtain a solution consisting of a mixture of aluminate and silicate.

The red mud residue from the Bayer process invariably contains soda and alumina. It may be fused with sodium carbonate and leached with water to obtain some soluble sodium aluminate, but, generally, such a process would not pay. Peffer[2] causticizes the red mud with lime in a digestor at 350°C. and recovers soluble soda.

Kendall[3] treats pulverized clay (which may be calcined) with sodium hydroxide under pressure, and after several hours' digestion opens the autoclave and adds milk of lime, and redigests for several hours. Levi[4] proposes to dissolve the alumina in silicates such as leucite, by treatment with concentrated sodium hydroxide and lime after part of the silica has been removed by digesting with alkali hydroxide or carbonate under 3 to 20 atmospheres' pressure. Peacock[5] digests feldspar, etc., with alkali carbonate at 5 atmospheres pressure to dissolve the silica and leave the alumina and iron in the residue for subsequent recovery. Jackson[6] digests clay with strong sodium hydroxide solution under pressure, and then attempts to separate alumina and silica by fractional precipitation with carbon dioxide; the assumption is that the alumina will precipitate first. He also proposes to precipitate alumina by adding freshly precipitated silica and then to remove the silica by dissolving it with sodium carbonate solution. Scofield and La Rue[7] treat calcined potash feldspar with strong potassium hydroxide solution in a digester

[1] Piva, A., Fr. Pat. 351,338, July 11, 1905.

[2] Peffer, H. C., U. S. Pat. 938,270, Oct. 26, 1909.

[3] Kendall, E. D., U. S. Pat. 1,013,022, Dec. 26, 1911.

[4] Levi, G., Fr. Pat. 344,296, Oct. 29, 1904; Ger. Pat. 174,698, Sept. 18, 1906; Br. Pat. 13,875 (1904) applied for June 18, 1904.

[5] Peacock, S., U. S. Pat. 1,030,122, June 18, 1912.

[6] Jackson, L. L., U. S. Pat. 1,305,969, June 3, 1919.

[7] Scofield, W. S., J. B. La Rue, U. S. Pats. 1,494,029, May 13, 1924; 1,563,875, Dec. 1, 1925; 1,483,627, Feb. 12, 1924.

at 300°C. and obtain soluble potassium silicate, potassium aluminate, and an insoluble potassium aluminum silicate. After diluting the solution, the alumina and silica are precipitated with carbon dioxide. Sulfuric acid decomposes the potassium aluminum silicate and dissolves the alumina but not the precipitated silica. By varying the treatment in the digester, the insoluble potassium aluminum silicate is not formed and practically all the material goes into solution.

In connection with these processes, it should be noted that the industry demands alumina containing not more than about 0.08 per cent silica, which is a limit not readily met by most processes. Practical experience with the Bayer process indicates that no separation of alumina from silica in an alkaline solution is practical, except by precipitating sodium aluminum silicate, so the processes described in the last paragraph seem to be of small value.

When alunite[1] is treated with barium hydroxide solution under pressure, soluble barium aluminate and insoluble barium sulfate are formed. The alumina is precipitated by cautious neutralization with hydrochloric acid, or alumina and barium carbonate may be simultaneously precipitated with carbon dioxide and the alumina leached out with caustic soda. Barium aluminate[2] may also be prepared by digesting bauxite with barium sulfide at 130°C. These processes would be too expensive to compete with the Bayer process.

Rankin[3] proposes to heat the ore with powdered alkali and water to a red heat under pressure. A process for the extraction of alumina from blast furnace slag[4] by means of sodium hydroxide under pressure has also been patented, but appears impractical.

From time to time various methods have been suggested which do not require a pressure digestion. Either a higher concentration of sodium hydroxide is employed in order to elevate the temperature of digestion,[5] or else the solution is hastened by special means, such as fine grinding, rapid agitation, etc. Melick[6] boils bauxite with saturated sodium or potassium hydroxide solution for two hours but finds it necessary to dilute the solution before filtering and precipitating. Muth[7] claims that a 97.6 per cent extraction of alumina is obtained when bauxite is boiled with enough 27 per cent sodium hydroxide

[1] HERSHMAN, P. R., U. S. Pat. 1,191,106, July 11, 1916.

[2] BERINGER, C. A., Ger. Pat. 347,374, Jan. 17, 1922.

[3] RANKIN, H. D., U. S. Pat. 1,471,751, Oct. 23, 1923.

[4] PARSONS, C. E., U. S. Pat. 1,522,698, Jan. 13, 1925.

[5] NEUMANN, B. and O. RENSCH, Z. angew. Chem., **39**, 1542 (1926).

[6] MELICK, W. L., U. S. Pat. 1,271,192, July 2, 1918.

[7] MUTH, G., Fr. Pat. 360,086, Apr. 12, 1906; Br. Pat. 25,477 (1905) Dec. 7, 1906; Can. Pat. 103,719, Feb. 19, 1907; Ger. Pat. 175,446, Sept. 21, 1906; Norw. Pat. 16,415, June 3, 1907; Swed. Pat. 22,900, Aug. 10, 1907.

olution to give a ratio of 1.7 mols Na_2O to 1 mol Al_2O_3. Dieffenbach[1] aims that a good extraction of the alumina in bauxite can be made by oiling with potassium hydroxide at 180 to 200°C, and that it is neces- ury to heat bauxite and sodium hydroxide to 350 to 500°C. in order to btain comparable results. To care for the silica, Tetéleni[2] adds 2 mols f CaO for each mol of silica present. The sodium hydroxide solution 45°Bé.) is boiled until a concentration of 50°Bé. is reached, and then, fter dilution, the alumina is fractionally precipitated.

Eustis[3] states that the alumina contained in Cuban iron ore can be xtracted by digesting the ore with strong sodium hydroxide solution.

The calcination of alumina at moderate temperatures (below 1000°C.) ives to it special properties; it absorbs water readily and can be used or drying gases.[4] Prager[5] claims that bauxites that do not ordinarily ermit a good extraction will work satisfactorily if they are first calcined nd then, while still hot, quenched in cold caustic soda. Another nethod of attack seems to be the use of a special homogenizer[6] in which he calcined bauxite is extracted for two hours at 120°C. The rapid gitation is said to favor the solution of the alumina at a lower tem- erature. Kleinmann[7] grinds the alumina in the presence of water with or without the addition of sodium hydroxide). The organic natter is destroyed and the iron oxidized to the ferric condition with odium hypochlorite. The alumina is then extracted with sodium ydroxide at 135°C. without pressure.

Grätzel[8] proposes to add bauxite directly to the cathode liquor of an lectrolytic cell in which aqueous sodium chloride is decomposed.

[1] DIEFFENBACH, O., U. S. Pat. 891,677, June 23, 1908; Br. Pat. 13,970 (1906) Jan. 17, 1907; Can. Pat. 102,718, Dec. 25, 1906; Fr. Pat. 367,728, Nov. 8, 1906; Ger. Pat. 182,775, Feb. 23, 1907; Norw. Pat. 16,620, Aug. 5, 1907.

[2] TETÉLENI, A., Swiss Pat. 73,101, Aug. 16, 1916; Ger. Pats. 299,652, 299,653, Oct. 4, 1919.

[3] EUSTIS, U. S. Pat. 1,237,765, Aug. 21, 1917.

[4] THIENEMANN, H., Ger. Pat. 405,238, Oct. 28, 1924.

MARDEN, J. W. and V. ELLIOTT., *J. Ind. Eng. Chem.*, **7**, 320 (1915).

MARDEN, J. W. and MARY V. DOVER, *J. Am. Chem. Soc.*, **39**, 1609 (1917).

YOE, J. H., *Chem. News*, **130**, 340 (1925).

JOHNSON, F. M. G., *J. Am. Chem. Soc.*, **34**, 911 (1912).

FISCHER, H. L., H. L. FAUST, and G. H. WALDEN, *J. Ind. Eng. Chem.*, **14**, 1138 (1922).

[5] PRAGER, A., Ger. Pat. 299,072, Feb. 23, 1918.

[6] SCHWEITZERISCHE SODAFABRIK, Ger. Pat. 355,301, June 21, 1922; Swiss Patent 96,474, Oct. 16, 1922.

[7] KLEINMANN, F., Br. Pat. 266,225, Feb. 25, 1927; Fr. Pat. 575,790, Aug. 6, 1924; Ger. Pat. 439,540, Jan. 15, 1927.

[8] GRÄTZEL, A., Fr. Pat. 243,428, June 12, 1894; Norw. Pat. 4,023, Sept. 7, 1895.

While the method is unique, any possible advantage obtained by the formation of the alkali hydroxide in situ does not seem to warrant its production by the electrolytic method, complicated by the presence of suspended solids in the cathode compartment. A somewhat similar proposal is that of Ikeda[1] to electrolyze a mixed solution of aluminum chloride and alkali chloride with the formation of alkali aluminate at the cathode.

Halvorsen[2] heats a mixture of alkali metal aluminum silicate and calcium cyanamide with superheated steam at 650°C., or with water in an autoclave under pressure and obtains ammonia as well as soluble alkali aluminate. It is said that the reaction is facilitated by the addition of salts such as chlorides, nitrates, and sulfates.

Lawrie[3] treats waste aluminous materials, such as dross, with sodium hydroxide to form an aluminate solution from which the other metal impurities are precipitated as sulfides, and the alumina is recovered in the usual manner.

Furnace Processes Using Alkali Carbonate or Hydroxide.

Solutions of sodium carbonate will not dissolve alumina, hence the necessity of "causticising" the carbonate by treatment with lime to convert it into hydroxide for use in the digestion of bauxite. Sodium carbonate, however, can be used directly in furnace processes where the ore, in intimate mixture with carbonates, is heated to a sufficiently high temperature. The reaction to form sodium aluminate liberates carbon dioxide and in effect "causticizes" the soda.

Barnitt[4] carries out this reaction by treating a mixture of bauxite, soda ash, and carbon on a sintering machine so that the carbon is burned out and leaves a porous clinker containing water-soluble sodium aluminate. This process has been operated commercially for the manufacture of dry sodium aluminate.

Petraeus[5] has proposed to use the spent caustic liquors from paper mills as a source of alkali for the fusion process. Le Chatelier[6] thought that the fusion of bauxite and kelp would produce sodium aluminate.

[1] IKEDA, S., Jap. Pat. 34,890, Sept. 11, 1919.

[2] HALVORSEN, B. F., U. S. Pat. 1,463,508, July 31, 1923; Br. Pat. 107,012, May 30, 1918; Fr. Pat. 486,577, Apr. 18, 1918; Norw. Pat. 27,883, Apr. 30, 1917; Swiss Pat. 77, 376, Apr. 1, 1918.

[3] LAWRIE, J. W., U. S. Pat. 1,228,119, May 29, 1917.

[4] BARNITT, J. B., U. S. Pat. 1,616,674, Feb. 8, 1927; Br. Pat. 264,823, May 5, 1927; Fr. Pat. 627,091, Sept. 26, 1927; Span. Pat. 101,144; Swed. Pat. 63,091; Ital. Pat. 255,776; Swiss Pat. 127,249, Aug. 16, 1928; Norw. Pat. 45,300, July 2, 1928.

[5] PETRAEUS, C. V., U. S. Pat. 312,894, Feb. 24, 1885.

[6] LE CHATELIER, Br. Pat. 1988 (1858) filed Mar. 1, 1859.

The difficultly soluble alumina obtained by roasting alunite can be made soluble by roasting with sodium carbonate at about 900°C.[1] Vergé[2] furnaces the bauxite with enough sodium carbonate to give a soda-alumina ratio of 1:1.1. Enough caustic soda is then added to increase the ratio to 1:1.6 and the product digested with water under pressure to remove the silica.

Beilby and Beilby[3] heat thin layers of sodium carbonate and aluminum oxide in an atmosphere of air or other indifferent gas. The bicarbonate of soda has also been used[4] for the formation of the alkali aluminates. The evolved carbon dioxide is collected and used for the precipitation of alumina.

It is difficult to extract the alumina from many clays without first breaking up the structure of the silicate. If clay is heated to a fairly high temperature, the alumina is easier to extract, apparently because the chemical bonds between the alumina, silica, and other constituents are weakened. It has been proposed that clay be furnaced with an alkali or alkaline earth, to decompose the silicate more completely.

Basset[5] calcines dried clay with an excess of sodium carbonate. After the material is crushed, it is leached with water, the silica precipitated with lime water, and the soluble alkali aluminate treated in the usual way. This would hardly give a practical separation. The addition of sodium chloride or sulfate[6] is said to insure the solubility of the potassium in the original material. Bassett states that by heating a mixture of 5 parts clay or feldspar with not over 3 parts sodium carbonate and 2 parts sodium chloride or sulfate to a red heat, he obtains a solution of alkali aluminate and potassium salt after the fused mass is digested with water. The sodium silicate ($2Na_2O.9SiO_2$) is said to be insoluble (!) and remains as a residue. In later patents Bassett[7] increases the amount of sodium carbonate until it is twice the weight of the feldspar. Enough sodium chloride or sulfate is added to replace the potassium and the mixture heated to a red heat for an hour. The potassium sulfate and sodium silicate are soluble while the sodium aluminum silicate is insoluble. The alumina is to be obtained from the double silicate by means of a solution of caustic soda containing a small amount of calcium and iron oxides. The lime is used to release the sodium and the iron oxide the aluminum. The lime and iron

[1] CHAPPELL, H. F., U. S. Pat. 1,270,266, June 25, 1918.

[2] VERGÉ, A., Fr. Pat. 373,070, Apr. 30, 1907.

[3] BEILBY, G. T., and H. N. BEILBY, Br. Pat. 18,750 (1907), Aug. 20, 1908.

[4] BRIVET, Fr. Pat. 244,429, Jan. 18, 1895.

[5] BASSET, A. M., Fr. Pat. 230,321, May 25, 1893; Add. Pat. June 30, 1894.

[6] BASSETT, H. P., U. S. Pat. 1,079,589, Nov. 25, 1913; 1,095,306, May 5, 1914.

[7] BASSETT, H. P., U. S. Pat. 1,404,083, Jan. 17, 1922; 1,410,642, Mar. 28, 1922.

oxide may be added to the original charge with a slight change in procedure. If it were possible thus to decompose sodium aluminum silicate, soda losses in the Bayer process would be much less.

Cochrane[1] prepares alkali aluminate by sintering blast furnace slag with alkali salt (carbonate). McCormack[2] heats Cuban ore (containing chromium, nickel, cobalt, etc.) with sodium carbonate and obtains alkali aluminate and chromate soluble in water. Carbon dioxide will precipitate the aluminum but not the chromium. Unfortunately tests indicate that extraction of the chromium is quite incomplete, and the silica present interferes with the extraction of the alumina.

Lindblad[3] heats feldspar with carbon and iron or copper in the electric furnace to remove part of the silicon as ferrosilicon and form a compound similar to leucite or to remove all the silicon and form potassium aluminate, which may be treated either with sulfuric acid to form potash alum, or with carbon dioxide to form alumina and potassium carbonate.

Furnace Processes Using Alkaline Earth Carbonate or Oxide.

Many processes have been proposed in which the ore— bauxite, for example— is fused with an alkaline earth carbonate so as to form the alkaline earth aluminate. Alumina can then be recovered from the alkaline earth aluminate or the aluminate may be used for other purposes, such as making a quick-setting cement. The use of an alkaline earth carbonate instead of sodium carbonate has the advantage, it is claimed, of eliminating loss of soda by volatilization.

A practical process of this type is that of Prof. Harald Pedersen.[4] Pedersen smelts a mixture of iron ore, coke, lime, and bauxite or other aluminous material to produce a molten calcium alu-

[1] COCHRANE, C., Br. Pat. 1883 (1862), sealed Oct. 31, 1862.

[2] McCORMACK, C. P., U. S. Pat. 1,575,852, Mar. 9, 1926; see also I. G. FARBENINDUSTRIE, A.-G., Br. Pat. 273,666, Jan. 12, 1928; Swiss Pat. 129,297, Dec. 1, 1928: Fr. Pat. 636,782, Apr. 16, 1928.

[3] LINDBLAD, A. R., Br. Pat. 23,898 (1912), Feb. 13, 1913.

[4] PEDERSEN, H., Br. Pat. 232,930, June 14, 1926; Fr. Pat. 596,400, Oct. 22, 1925; Swiss Pat. 115,356, July 1, 1926; Norw. Pat. 43,415, Nov. 22, 1926; Ital. Pat. 238,488; Portuguese Pat. 14,145; Span. Pat. 93,555; Roumanian Pat. 11,568; Australian Pat. 22,793 (1925), Mar. 23, 1926; Indian Pat. 11,203; Mexican Pat. 24,720; Finnish Pat. 11,609; Hungarian Pat. 91,203; Jugo-Slavian Pat. 4,358; Polish Pat. 4,504; Br. Guiana Pat. 190, June 11, 1925; Aust. Pat. 108,109, Nov. 25, 1927. See also BONTHRON, J. A., T. R. HAGLUND, Can. Pat. 284,109, Oct. 23, 1928; Fr. Pat. 643,024, Sept. 8, 1928.

minate slag containing 30 to 50 per cent of alumina and only 5 to 10 per cent silica. Low-sulfur iron of a high grade is produced as a by-product. The alumina in the slag can be extracted
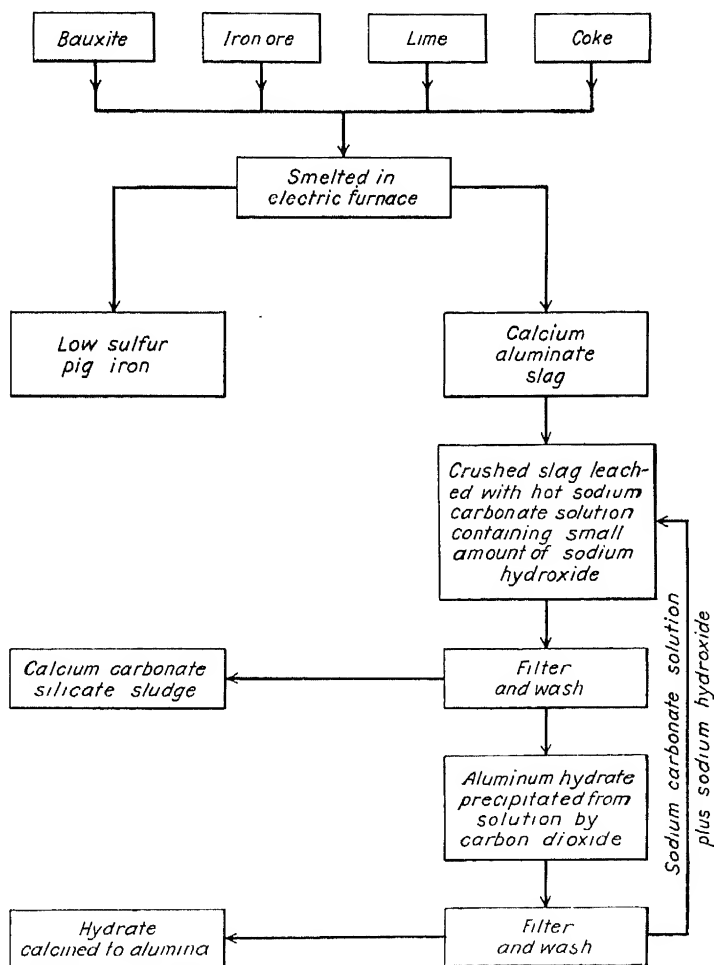
Fig. 38. Diagram of Pedersen process for producing alumina.

by means of a sodium carbonate solution which forms insoluble calcium carbonate and soluble sodium aluminate. Pedersen[1]

[1] PEDERSEN, H., U. S. Pat. 1,618,105, Feb. 15, 1927; Br. Pat. 252,399, June 9, 1927; Fr. Pat. 616,395, Feb. 1, 1927; Can. Pat. 269,220, Mar. 22, 1927; Norw. Pat. 44,305, Aug. 15, 1927; Indian Pat. 12,353; Br. Guiana Pat. 203; Ital. Pat. 249,337; Span. Pat. 98,244; Roumanian Pat. 12,889; Brazilian

finds that a 3 to 8 per cent solution of sodium carbonate containing about 0.3 to 0.8 per cent sodium hydroxide can be effectively used for extracting the calcium aluminate slag. Commercial operation of this process began in 1928 at Høyanger, Norway.

Calcium aluminate slags of the type used by Pedersen have been satisfactorily produced in a blast furnace by Joseph, Kinney, and Wood,[1] of the U. S. Bureau of Mines, in cooperation with the Research Bureau of Aluminum Company of America.

The temperature of fusion can be lowered by controlling the amount of lime, for there are several calcium aluminates,[2] and they form low-melting eutectics. Koritschoner and Hansgirg recommend that the silicon and iron should be in the ratio of 1:4 and that they be reduced by carbon during the fusion and removed as an alloy of iron and silicon.

Other proposals along this line have been made by Peffer[3] who calcines a mixture of lime and bauxite at red heat and then digests the resulting calcium aluminate with sodium carbonate solution. The soluble alkali aluminate is then treated by known methods. Lambert[4] fuses lime and bauxite in the electric furnace and then leaches the product with hot sodium carbonate solution. Heating the limestone and bauxite in two steps[5] is said to give better combination and higher alumina extraction. Carbon[6] and other reducing agents may be added to the mixture of bauxite and limestone which is to be fused in the electric furnace. The oxides of iron, titanium, and silicon are reduced and a ferro-alloy separates, leaving a purer calcium aluminate.

Williams and Sims[7] treated clay by the Miguet process but were unable to secure a satisfactory extraction of alumina from the slag,

Pat. 15,805; Mexican Pat. 26,770; Portug. Pat. 14,576; Australian Pat. 2,541 (26) July 12, 1927; Swiss Pat. 127,248, Aug. 16, 1928; Polish Pat. 6595; Finnish Pat. 12,137, Aug. 29, 1928.

[1] JOSEPH, T. L., S. P. KINNEY and C. E. WOOD, *Am. Inst. Mining Met. Eng., Tech. Pub.* 112, 1928.

[2] KORITSCHONER, J., and F. HANSGIRG, Br. Pat. 199,017, Sept. 1, 1921; Fr. Pat. 567,046, Feb. 23, 1924.

[3] PEFFER, H. C., U. S. Pat. 826,354, July 17, 1906.

[4] LAMBERT, A., Fr. Pat. 477,988, Nov. 18, 1915.

[5] SOCIÉTÉ ELECTROMÉTALLURGIQUE FRANÇAISE, Br. Pat. 146,133, Aug. 4, 1921; Fr. Pat. 501,835, Apr. 27, 1920; Ger. Pat. 343,264, Oct. 29, 1921; Swed. Pat. 48,979, Jan. 19, 1920; Swiss Pat. 93,574, Mar. 16, 1922.

[6] MIGUET, P., U. S. Pat. 1,376,563, May 3, 1921; ROCHETTE FRÈRES, Br. Pat. 141,666, Sept. 30, 1920; Fr. Pat. 519,819, June 16, 1921; Add. Pat. 23, 636, Dec. 14, 1921.

See also TERAZAKI, K., and T. SAKI, Jap. Pat. 37,489, Nov. 22, 1920.

[7] WILLIAMS, C. E. and C. E. SIMS, *U. S. Bur. Mines Reps. Investig.*, 2393 (1922).

resumably because of the presence of silica. Peacock[1] adds to feldspar nough lime to combine with the silica, and heats the mixture to 1400°C.; nost of the potash is said to be removed by volatilization. The alumina s then extracted by digesting with an alkali solution under pressure. Experience with other processes indicates that the alkali would also ttack the calcium silicate, causing loss of alumina and soda. Rody[2] eats feldspar or leucite with an alkaline earth metal oxide to a sintering emperature and then extracts the soluble alkali aluminate. Jourdan[3] eats leucite and calcium carbonate to 1000 to 1400°C. and then eparates the resulting insoluble calcium silicate and soluble potassium luminate by means of water. In a later patent,[4] he states that iron arbonate acts as a good flux and that if the fused mass is cast into arge blocks and allowed to cool slowly, the blocks will spontaneously isintegrate and fall apart and at the same time give a higher potash xtraction.

Lambert[5] heats an ore of aluminum with a proportionate amount f alkaline earth oxide or carbonate to form the normal aluminate. Barium aluminate is soluble in water, while calcium aluminate is nsoluble. In either case the melt is treated with a solution of sodium arbonate or sulfate and a solution of alkali aluminate is obtained ractically free of silica (?). Tyrer[6] adds 2 mols of lime for each mol f silica and 1 for each mol of alumina. After fusion, the melt is xtracted with sodium carbonate solution. With higher molar ratios f an alkaline earth oxide, Seailles[7] claims that the aluminous ore may e decomposed in a digester in the presence of water to form alkaline arth aluminate. It is preferable to use very finely ground material nd to heat under pressure. Kayser[8] makes an artificial sodium-silico-luminate which is decomposed by furnacing with lime. The soluble lkali aluminate is treated in the ordinary manner. Lindblad[9] decom-oses naturally-occurring alkali aluminum silicates by heating with

[1] PEACOCK, S., U. S. Pats. 1,035,812, Aug. 13, 1912; 1,036,897, Aug. 27, 912.

[2] RODY, F. A., U. S. Pats. 1,151,533, Aug. 24, 1915; 1,263,705, Apr. 23, 918.

[3] JOURDAN, F., Fr. Pat. 527,066, Oct. 20, 1921; Br. Pat. 195,084 (void) pplied for Mar. 16, 1923.

[4] JOURDAN, F., U. S. Pat. 1,620,212, Mar. 8, 1927; Br. Pat. 226,819, une 18, 1925; Ger. Pat. 425,797, Mar. 2, 1926; Fr. Pats. 556,993, Aug. 1, 923; 591,043, June 26, 1925.

[5] LAMBERT, A. D. A., Fr. Pat. 382,347, Feb. 4, 1908.

[6] TYRER, D., Br. Pat. 172,087, Nov. 24, 1921.

[7] SEAILLES, J. C., Br. Pats. 277,697, Jan. 26, 1928; 283,509, June 21, 928; Fr. Pats. 634,430, Feb. 17, 1928 649,029 Dec. 17, 1928.

[8] KAYSER, A., U. S. Pat. 454,137, June 16, 1891.

[9] LINDBLAD, A. R., Swed. Pat. 51,522, Apr. 26, 1922.

lime in an electric furnace under reduced pressure, the alkali compounds being volatile.

Furnace Processes Using Both Alkali and Alkaline Earth Carbonates.

An alkaline earth aluminate formed by fusing alumina and an alkaline earth carbonate or oxide may be changed into alkali aluminate by treating the product of the fusion with alkali solution as above described. The alkali may also be added directly to the charge before it is fused and the extraction made with water. The probability that some silica will be dissolved and considerable soda and alumina precipitated, must not be overlooked in considering these processes. Collett[1] melts a mixture composed of bauxite, alkaline earth metal oxide, and sodium carbonate in an electric furnace. The molten material is run into water or allowed to cool. In either case, it is easily broken up and alumina can be extracted with sodium carbonate solution. It is claimed[2] that the yield of alumina is high and the silica content low when bauxite is fused with sodium carbonate and a mixture of barium and calcium carbonates. The high cost of barium carbonate would be a considerable handicap. When an aluminum silicate[3] is heated with calcium oxide and sodium hydroxide, the alkali aluminate formed may be extracted with water. Kayser[4] fuses marl with the addition of sodium carbonate; there is calcium carbonate already present in the marl. Packard[5] fuses clay with sodium and calcium carbonates. He uses 2 mols of Na_2O for each mol of Al_2O_3 and 2 mols CaO for each mol SiO_2.

Jebsen and Witt[6] grind feldspar intimately with enough limestone to combine with all the silica present and add potassium carbonate to serve as a flux. The potassium aluminate formed by heating is soluble in water. Rody[7] claims that enough alkaline earth oxide should be added to feldspar or leucite to form the alkaline earth ortho-silicate and enough alkali to give 1.7 mols alkali for each mol of alumina. He also says[8] that the presence of iron oxide decreases the required amounts

[1] COLLETT, E., Ger. Pat. 377,664, June 23, 1923.

[2] ELECTRO-METALLURGIE DU SUD-EST, Fr. Pat. 389,008, Aug. 28, 1908.

[3] SOCIETÀ ROMANA SOLFATI, Fr. Pat. 352,275, Aug. 7, 1905; MUELLER, H., Ger. Pat. 12,947, Mar. 24, 1881; LANGLET, N. A., Swed. Pat. 25,370, Aug. 29, 1908; RODY, F. A., and H. M. BURKEY, U. S. Pat. 1,151,498, Aug. 24, 1915; Br. Pat. 17,985 (1904), Sept. 18, 1905.

[4] KAYSER, A., U. S. Pat. 708,561, Sept. 9, 1902; Can. Pat. 84,871, Jan. 19, 1904.

[5] PACKARD, M., Br. Pat. 20,220 (1902) Nov. 13, 1902; Ger. Pat. 182,442, Mar. 14, 1907.

[6] JEBSEN, G. and O. WITT, Norw. Pat. 19,931, Mar. 14, 1910.

[7] RODY, F. A., U. S. Pat. 1,285,796, Nov. 26, 1918.

[8] RODY, F. A., U. S. Pat. 1,495,498, May 27, 1924.

of alkali and alkaline earths. Martin[1] heats aluminous earths with calcium carbonate and a small amount of alkali salt, preferably sulfate. The mixed aluminates are digested at 80°C. with a carbonate solution partly saturated with aluminate. It is said that very little silica is present in the final product when the counter-current system of digestion is used. Considerable large scale experimental work was done with this process, but it was not successful. The furnacing step gave trouble, and silica went into solution and contaminated the alumina. Sherwin[2] sinters a low-grade ore, or red mud, with lime and a sodium compound, and leaches with caustic soda or residual soda liquor from the Bayer process. The temperature of digestion should not exceed 200°F., since a higher temperature causes the formation of insoluble compounds of soda, alumina and silica. Semi-commercial experiments with this process did not give economically advantageous results. Cowles[3] states that in the ordinary fusion of an alkali silico-aluminate, 2 mols of soda are used for each mol of alumina and 2 mols of lime for each mol of silica. He claims that a soda-alumina ratio of from 1.1 to 1.76 gives good results and that, although the furnaced product dissolves at a slower rate, the alumina can be precipitated more readily from the aluminate solution.

Askenasy and Gerber[4] heat clay with barium carbonate (1 BaO to Al_2O_3) and calcium carbonate (2CaO to $1SiO_2$) and sodium chloride. The resulting barium aluminate is soluble in water and contains no iron and little silica. The barium aluminate solution is treated in the regular manner with sodium carbonate or sulfate solution. It is claimed[5] that an artificial product such as an aluminous slag can be used with lime and alkali carbonate to form soluble alkali aluminate.

Furnace Processes Using Sulfides or Sulfates.

The furnace process for the formation of alkali aluminate becomes somewhat more complicated when sodium sulfate is substituted for the hydroxide or carbonate, in order to reduce the cost of the alkali. The first step in the reaction consists in

[1] MARTIN, E., U. S. Pat. 1,394,854, Oct. 25, 1921; Br. Pat. 9,662 (1915) Nov. 18, 1915; Fr. Pat. 475,476, May 18, 1915; Ger. Pat. 332,389, Feb. , 1921; Swed. Pat. 47,962, June 30, 1919; Swiss Pat. 89, 956, July 16, 1921; Norw. Pat. 33,535, Nov. 14, 1921.

[2] SHERWIN, R. S., U. S. Pat. 1,422,004, July 4, 1922.

[3] COWLES, A. H., U. S. Pats. 1,508,777, Sept. 16, 1924; 1,514,657, Nov. 1, 1924; 1,591,364, July 6, 1926; 1,591,365, July 6, 1926; Br. Pat. 107,640, July 4, 1917.

[4] ASKENASY, P., V. GERBER, Ger. Pat. 306,355, Dec. 15, 1920; see also *Electrochem.* **25**, 193 (1919).

[5] METALLBANK UND METALLURGISCHE GESELLSCHAFT, A.-G., Ger. Pat. 55,302, June 24, 1922.

converting the sulfate to sulfide or oxide either directly in the charge or in another furnace. This is usually accomplished by heating the sulfate with carbon so that oxides of sulfur and carbon are formed. The sulfur gases evolved during the reaction must be conducted away, and, if possible, converted into other compounds or used for another step in the process. Their dilution, however, makes recovery difficult and expensive.

When a mixture of alumina and sodium sulfide is heated in the presence of superheated steam,[1] hydrogen sulfide and soluble alkali aluminates are said to be formed. If air is substituted for the steam, sulfur dioxide is formed as a by-product. It is stated by Siermann[2] that alumina in the presence of air will react with alkali sulfate at red heat to form alkali aluminate and oxides of sulfur. In order to cause a more complete decomposition, Hershman[3] adds lime to a mixture of barytes and alumina which is heated to 1000°C. in the presence of steam. The resulting barium aluminate is soluble in hot water. It is apparently good practice[4] to add enough lime to the bauxite or other aluminous material to convert the silica to orthosilicate. The mixture of lime, bauxite, and alkali sulfate is heated to 1100°C. in the presence of steam to form the soluble alkali aluminate and insoluble calcium orthosilicate.

As was previously stated, the more general practice is to add carbon to the sulfate and alumina mixture. The alkali sulfate may be completely reduced by the carbon to form alkali sulfide and carbon monoxide or dioxide, depending upon the quantities used and the temperatures employed. Müller[5] specifically controls the conditions so that carbon monoxide is formed. To avoid the formation of sulfide, Peniakoff[6] adds only one-quarter the amount of carbon necessary to completely reduce the sulfate and obtains sulfur dioxide and carbon dioxide. Emery[7] produces the same results by fusing the mixture of bauxite, sodium sulfate, and carbon in excess air. Peniakoff[8] describes a con-

[1] WELDON, W., Br. Pats. 3,385 (1876) Nov. 24, 1876; 3,386 (1876) applied for Aug. 28, 1876; COMPAGNIE GÉNÉRALE L'ALUMINE, Br. Pat. 8,072 (1896) May 23, 1896.

[2] SIERMANN, E., Br. Pat. 356 (1878) Jan. 28, 1878; Ger. Pat. 3.280, Jan. 18, 1878.

[3] HERSHMAN, P. R., U. S. Pat. 1,240,572, Sept. 18, 1917.

[4] RHENANIA VEREIN CHEMISCHER FABRIKEN A.-G., Br. Pat. 241,232, June 24, 1926; Fr. Pat. 605,330, May 25, 1926; Swiss Pat. 120,253, May 16, 1927; ROTHE, F., H. BRENEK, U. S. Pat. 1,680,066, Aug. 7, 1928.

[5] MÜLLER, H., Ger. Pat. 230,118, Jan. 16, 1911.

[6] PENIAKOFF, D. A., U. S. Pat. 603,657, May 10, 1898; Br. Pat. 22,038 (1895) Sept. 19, 1896; Ger. Pat. 93,952, Sept. 2, 1897.

[7] EMERY, S. S., U. S. Pat. 818,754, Apr. 24, 1906.

[8] PENIAKOFF, D. A., Br. Pat. 14,707, (1908) Mar. 4, 1909; Fr. Pat. 396,5 Apr. 15, 1909; Ger. Pat. 247,763, June 6, 1912; Can. Pat. 129,434, Nov. 22, 1910.

nuous process wherein a mixture of bauxite, carbon, and sodium
lfate or sulfide is fed into a revolving tube furnace, which is heated
y burning gas or carbon in the interior of the furnace. A higher
)ncentration of sulfur dioxide in the resulting gases is claimed. It is
nderstood that the Peniakoff plant in Belgium operated on a sodium
lfate fusion process before the World War.
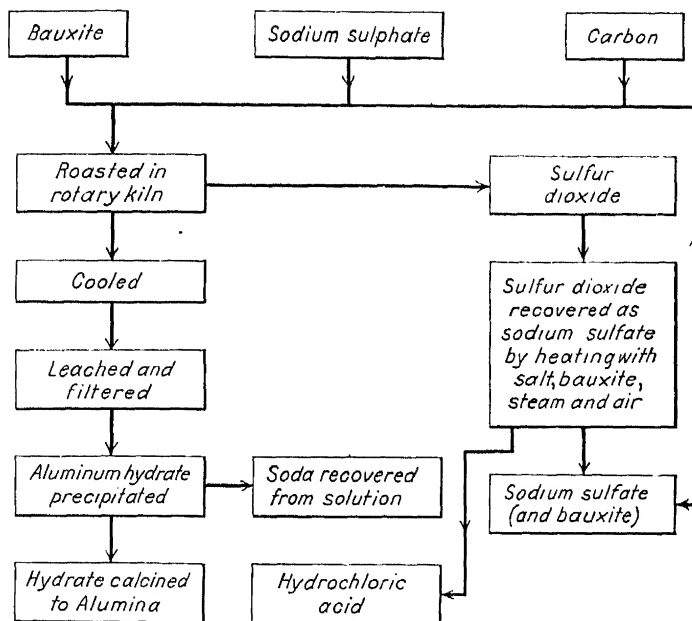
FIG. 39.—Diagram of Peniakoff process for producing alumina.

The presence of iron appears to play a more important role in the
lfate furnace process than in the simple aluminate process. For
stance, iron oxide or iron[1] may be added to the reaction mixture
combine with the sulfur as iron sulfide. This iron sulfide may become
ry troublesome, however, since it easily forms colloidal solutions or
uble double sulfides in the presence of sodium sulfide, contaminating
; aluminate solution. Behnke[2] heats a mixture of bauxite, carbon,
.ali sulfate, and iron (one equivalent of iron as iron oxide for each two
.uivalents of sulfate) to a high temperature. He says that iron
fide remains insoluble when the mass is treated with water. It is

PROJAHN, F., U. S. Pat. 684,864, Oct. 22, 1901; Ger. Pat. 112,173,
ie 9, 1900; Austr. Pat. 1,310, May 10, 1900; Br. Pat. 6,790 (1899), Mar.
1900.
BEHNKE, J. H. C., Ger. Pat. 7,256, Apr. 1, 1879.

also stated by Raynaud[1] that the oxides of iron do not interfere. In this case, however, steam is passed over the red-hot briquetted mixture and the sulfur eliminated as sulfur or hydrogen sulfide. Fleischer[2] adds enough iron oxide to the mixture of alkali sulfate, bauxite, and carbon to combine with the sulfur. An excess of lime over that required to combine with the silica is also added, resulting in the formation of an insoluble double sulfide of iron and calcium, and avoiding the soluble sodium and iron sulfide complex. Müller[3] heats a mixture of alumina, sodium sulfate, calcium carbonate, iron and sulfur and then extracts the sinter with sodium hydrosulfide solution and leaves as an insoluble residue the calcium silicate and a double sulfide of calcium and iron.

Bihn[4] treats the alkali aluminate solution with metallic copper, copper oxide, or oxysulfide and removes in this way the sulfides that are present in the solution. Freist[5] precipitates the iron by means of a metallic peroxide, sesquioxide, or "hyperoxide." Clemm[6] intentionally forms an excess of alkali sulfide by fusing a mixture of bauxite, alkali sulfate, and carbon. The alumina is precipitated with sulfur dioxide or hydrogen sulfide gas, and alkali thiosulfate or sulfhydrate obtained as a by-product. After adding enough sodium sulfate to form sulfide with the iron in a mixture of bauxite and iron oxide, Laur[7] adds a sufficient quantity of sodium carbonate or hydrate to form a compound which he gives as $Na_6Al_4O_9$. This aluminate, he says, is more stable than the normal aluminate ($NaAlO_2$) and is extracted by water under a pressure which corresponds to a temperature of 140 to 150°C. Claus[8] heats a mixture of bauxite and alkali sulfate in a reducing atmosphere and obtains alkali aluminate and hydrogen sulfide.

Barium sulfate is sometimes used in place of the alkali sulfate. Tedesco[9] heats a mixture of alumina, barium sulfate, and carbon to a red heat. The barium aluminate is dissolved in water and the barium precipitated as sulfate with alkali sulfate. Pernot and Guirard[10] vary the procedure somewhat and after first heating a mixture of bauxite,

[1] RAYNAUD, F., U. S. Pat. 612,364, Oct. 11, 1898; Norw. Pat. 5,306, Mar. 29, 1897; Swed. Pat. 8,170, Aug. 14, 1897; Dan. Pat. 1,483, Feb. 22, 1898.

[2] FLEISCHER, E., U. S. Pat. 472,668, Apr. 12, 1892; Br. Pat. 7,437 (1891) Feb. 13, 1892; Ger. Pat. 62,265, Apr. 25, 1892.

[3] MÜLLER, H., Ger. Pat. 230,118, Jan. 16, 1911.

[4] BIHN, G. F., U. S. Pat. 331,182, Nov. 24, 1885.

[5] FREIST, H. C., U. S. Pat. 328,478, Oct. 20, 1885.

[6] CLEMM, A., U. S. Pats. 845,854, Mar. 5, 1907; 848,612, Mar. 26, 1907; Br. Pat. 5,478 (1906) Mar. 6, 1907; Ger. Pats. 180,554, Jan. 24, 1907; 185,030, May 14, 1907; Fr. Pat. 363,893, Aug. 9, 1906.

[7] LAUR, F., Ger. Pat. 52,726, July 12, 1890.

[8] CLAUS, C. F., Br. Pat. 4,311 (1891) Mar. 10, 1891.

[9] TEDESCO, A., Ger. Pat. 19,767, Oct. 9, 1882.

[10] PERNOT, L. and J. GUIRARD, Fr. Pat. 405,891, Jan. 15, 1910.

barium sulfate, and carbon to a red heat until the sulfate is reduced to sulfide, they pass steam and carbon dioxide over the material, forming hydrogen sulfide and barium carbonate. The barium carbonate and alumina react to form soluble barium aluminate. Hydrogen sulfide precipitates alumina from this solution and forms soluble barium sulfide. Hershman[1] heats a mixture of alumina, barium sulfate, and excess carbon in the presence of reducing gas and steam at a temperature of 1000 to 1100°C. Soluble barium aluminate and free sulfur are formed.

The sulfate process has been suggested for application to aluminous materials other than alumina or bauxite. For instance, when soda alum is fused with carbon,[2] the product is $Al_2O_3.3Na_2S$. The addition of 3 mols of quicklime results in the formation of soluble sodium aluminate and insoluble calcium sulfide. Takeshima[3] roasts with carbon a mixture of aluminum silicate, 2 mols calcium carbonate for each mol of silica, and 2 mols sodium sulfate for each mol of alumina, and after steeping the mixture in water obtains a solution of sodium aluminate. Beringer[4] states that a mixture of clay, barium sulfate, lime and carbon should be heated for 8 hours at a red heat (1200°C.). The barium aluminate in the furnaced product is soluble in hot water and the calcium silicate is insoluble. An insoluble alkaline earth silicate is formed, according to Borchers,[5] when clay is furnaced with an alkaline earth sulfate in the presence of a reducing agent and steam. The alumina is in a form which is readily extracted either by furnacing with soda or by treating with a solution of alkali.

In addition to the reducing agents which have been mentioned for the reduction of the alkali and alkaline earth sulfates in the production of aluminates by the furnace process, there still remains another class to be considered, and that is the sulfides.

The reaction between sulfide and sulfate produces sulfur dioxide, which has many industrial uses. Peniakoff[6] patented a process in which bauxite is fused with a mixture of alkali sulfate and one-fifth of its weight of alkali sulfide. The products of the reaction are soluble alkali aluminate and pure sulfur dioxide. If iron pyrites is substituted for the alkali sulfide, the reaction is more energetic and iron oxide is

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[1] HERSHMAN, P. R., U. S. Pat. 1,240,571, Sept. 18, 1917.

[2] EMANUEL, P. A., Br. Pat. 20,047 (1910); 20,048 (1910) Void.

[3] TAKESHIMA, Y., U. S. Pat. 1,277,503, Sept. 3, 1918.

[4] BERINGER, C. A., Ger. Pat. 275,287, June 13, 1914.

[5] BORCHERS, W., Ger. Pats. 300,092, Aug. 9, 1919; 300,684, Mar. 15, 1920.

[6] PENIAKOFF, D. A., U. S. Pat. 572,026, Nov. 24, 1896; Br. Pat. 20,604, (1893) Aug. 18, 1894; Fr. Pat. 229,154, Apr. 5, 1893; Swed. Pat. 5,986, Apr. 27, 1895.

formed as a by-product. According to Peniakoff,[1] the iron is present in red bauxite as Fe_2O_3. After the bauxite is fused with sulfate and sulfide, the iron is present as FeO. In other words, part of the oxygen in the ferric oxide can react with the sulfide to form sulfur dioxide. He takes this fact into consideration in calculating the relative amounts of the materials in the charges. Barium sulfate (or strontium sulfate) may be calcined with alumina and a sulfide,[2] such as iron pyrites or barium sulfide, to form sulfur dioxide and soluble barium aluminate.

Chlorides have been used in conjunction with sulfates. For instance, Lieber[3] heats alumina with sulfuric acid and sodium chloride. The first reaction is said to result in the formation of hydrochloric acid and sodium sulfate. Superheated steam, hydrogen, or a hydrocarbon is passed over the heated mixture after the hydrochloric acid is all evolved. In another patent, Lieber[4] heats aluminous material with magnesium sulfate and alkali chloride in the presence of air or steam. Chlorine or hydrochloric acid is first evolved, and then sulfur dioxide. Beringer[5] forms barium aluminate by heating alumina with barium sulfate and hydrochloric acid or a metallic chloride and conducting steam over the heated mass.

Furnace Processes Using Alkali or Alkaline Earth Chlorides.

The alkali and alkaline earth chlorides may be used to form aluminates. The alumina and chloride are heated to a high temperature and air or steam passed over the red-hot mixture. The chloride is decomposed under these conditions, forming chlorine when air is used and hydrochloric acid when steam is used. According to Clews,[6] the following three reactions were observed at temperatures of 830 to 1050°C. and in the presence of moist air:

$A.$ $4x \ NaCl + y \ Al_2O_3 + x \ O_2 = 2x \ Na_2O.y \ Al_2O_3 + 2x \ Cl_2.$
$B.$ $2x \ NaCl + y \ Al_2O_3 + x \ H_2O = x \ Na_2O.y \ Al_2O_3 + 2x \ HCl.$
$C.$ $4 \ HCl + O_2 = 2H_2O + 2Cl_2.$
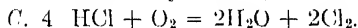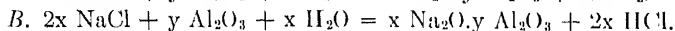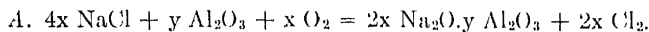
Reaction B appeared to predominate, the evidence being that the chlorine formed results more from reaction C than A. Reaction B is reversible at about 1000°C. For complete reaction with the NaCl, an excess of Al_2O_3 is more important than an excess of H_2O. Early

[1] PENIAKOFF, D. A., Br. Pat. 22,039 (1895) Sept. 19, 1896; Ger. Pats. 80,063, Feb. 12, 1895; 93,857, Aug. 25, 1897.

[2] PENIAKOFF, D. A., Br. Pat. 6,096 (1896) applied for Nov. 19, 1896.

[3] LIEBER, K. G., Br. Pat. 2183 (1877) applied for June 5, 1877; Ger. Pats. 1049, July 12, 1877; 1736, Dec. 11, 1877.

[4] LIEBER, K. G., Ger. Pat. 5610, Nov. 26, 1878.

[5] BERINGER, C. A., Ger. Pat. 244,221, Mar. 4, 1912.

[6] CLEWS, F. H., J. Chem. Soc., 127, 735 (1925).

British patents to Gossage,[1] Weldon,[2] Grüneberg and Vorster[3] and Hackspill and Salomon[4] describe the reaction between sodium chloride, alumina, and steam.

Although he does not add steam as such, Blackmore[5] specifically states that hydrated aluminum oxide can be added to molten sodium chloride in order to form hydrochloric acid and sodium aluminate. Lichtenberger and Flor[6] heat a mixture of salt and alumina to a temperature of 500 to 600°C. in the presence of steam. They state that a porous product is obtained when 6 mols of salt are used for each mol of alumina and that salts of manganese, copper, chromium, magnesium, etc., act as catalysts. A continuous process is described by Peniakoff,[7] in which a mixture of salt, red bauxite, and a small amount of carbon is submitted to a gradually increasing heat under the combined action of a mixture of water vapor, sulfur dioxide, and air, or even sulfur dioxide and air only. The iron in the bauxite acts as a carrier of sulfur dioxide by the intermediate formation of sulfate and chloride. After the reaction is once started it is necessary to add sulfur dioxide only to replace the unavoidable losses. The alkali aluminate is discharged from the hot end of the kiln and the chlorine and hydrochloric acid from the cold end. The carbon is added to reduce the alkali sulfate which is supposed to be formed as an intermediate product during the reaction. Solvay[8] heats a mixture of aluminum silicate and calcium chloride in the presence of air or steam. The resulting calcium aluminate and silicate are decomposed by chlorine or hydrochloric acid to give soluble chloride and a mixture of insoluble silica and alumina. According to Hall,[9] a mixture of calcium and sodium chlorides may be fused with bauxite in an atmosphere of air or steam to form calcium aluminate which can then be extracted with alkali carbonate solution. Simon and Pernot[10] heat bauxite, lime and carbon in the presence of steam with enough sodium chloride so that sodium

[1] Gossage, W., Br. Pat. 2050 (1862) applied for July 18, 1862.

[2] Weldon, W., Br. Pat. 2768 (1866) applied for Oct. 26, 1866.

[3] Grüneberg, H. and J. Vorster, Br. Pat. 2639 (1874) applied for July 28, 1874.

[4] Hackspill, L., and J. Salomon, *Chimie et Industrie Special* No. 415 6, April, 1928.

[5] Blackmore, H. S., U. S. Pat. 618,772, Jan. 31, 1899.

[6] Lichtenberger, T. and K. Flor, Br. Pat. 231,147, Nov. 26, 1925; Fr. Pat. 593,497, Aug. 24, 1925.

[7] Peniakoff, D. A., U. S. Pat. 1,045,097, Nov. 19, 1912; Br. Pat. 30,324, (1909) Nov. 10, 1910; Fr. Pat. 420,461, Jan. 31, 1911; Swed. Pat. 21,592, Nov. 22, 1916; Norw. Pat. 21,885, Dec. 4, 1911; Austrian Pat. 48,993, July 25, 1911.

[8] Solvay, E., Br. Pat. 171 (1877) applied for Jan. 12, 1877.

[9] Hall, C. M., U. S. Pat. 921,609, May 11, 1909.

[10] Simon, A., and L. Pernot, Fr. Pat. 405,135, Dec. 20, 1909.

aluminate is formed directly. They propose to use the hydrochloric acid to form aluminum chloride, which is added to the alkali aluminate solution to precipitate alumina.

Not satisfied with a simple thermal process, Gat[1] proposes to electrolyze molten sodium chloride in a special furnace and allow the sodium vapors to react with bauxite. It is stated that the sodium vapors react with iron oxide to form sodium oxide, which reacts with the alumina to form sodium aluminate. Sodium silicate is also formed and has to be separated from the aluminate. This method is novel in that it departs from the regular procedure of using air or steam to remove the chlorine from the bauxite, chloride, and carbon mixture, but is thoroughly impracticable. Another novel procedure is that suggested by Dutt.[2] Arsenic trioxide is passed over a red-hot mixture of bauxite, chloride, and carbon and the chlorine is removed as volatile arsenic trichloride.

Klein[3] says that he passes superheated steam through a fused mass of clay or bauxite and sodium chloride and obtains soluble alkali aluminate and hydrochloric acid. According to a German patent,[4] it is possible to extract the soluble alkali after clay and calcium chloride are heated to a "red heat" in the presence of air or steam. The alumina-containing residue is treated with hydrochloric acid and then heated to 120 to 130°C. The silica becomes insoluble and the chlorides of calcium and aluminum may be dissolved in water. Aluminum chloride is changed into the oxide when heated at 300°C. in the presence of air, while the calcium chloride remains unchanged and can be dissolved in water. In order to form mixed silicates for the manufacture of glass, Frink[5] furnaces a silicate such as feldspar with sodium chloride in the presence of steam and waste gases containing carbon monoxide and dioxide with sulfur dioxide, sulfur trioxide, and water. A limited quantity of lime is added to the hot mixture with the formation of mixed silicates, soluble sulfates, and aluminates of the alkali metals.

According to Kayser,[6] an acid sodium silicoaluminate is formed by heating bricks or cakes of clay and salt in the presence of steam. A high

[1] Gat, J. D., U. S. Pat. 1,478,822, Dec. 25, 1923; Ger. Pat. 359,926, Oct. 17, 1922; Norw. Pat. 40,179, Nov. 10, 1924; Br. Pat. 174,908, Dec. 21, 1922.

[2] Dutt, E. E., U. S. Pats. 1,332,113, 1,332,115, Feb. 24, 1920; Br. Pats. 118,155, 118,156, Aug. 19, 1918; 124,553, 124,554, Mar. 24, 1919; 123,243, Feb. 20, 1919; 120,838, Nov. 28, 1918; 119,261, Sept. 23, 1918.

[3] Klein, P. Fr. Pat. 368,106, Nov. 19, 1906; Can Pat. 102,617, Dec. 18, 1906.

[4] Chenal, Ferron, Douillet et Cie, Ger. Pat. 106,716, Nov. 3, 1899.

[5] Frink, R. L., U. S. Pat. 1,497,263, June 10, 1924; Br. Pat. 215,810, May 15, 1924.

[6] Kayser, A., U. S. Pats. 376,409, Jan. 10, 1888; 454,136, June 16, 1891; Br. Pats. 10,202 (1891) Oct. 10, 1891; 11,492 (1887) Sept. 23 '1887.

percentage of alumina is necessary so that the cakes do not fuse and form a solid mass. After the first reaction is completed, the acid sodium silicoaluminate is converted into the basic salt by melting in a furnace with alkali. The hydrous sodium silicoaluminate remains as a residue after treating with water and can be decomposed into soluble sodium aluminate and insoluble calcium silicoaluminate by heating with lime. Cowles[1] has made a number of improvements in this process. The reaction mixture is fed into a tunnel furnace in the form of briquets, to which carbon has been added to aid combustion and make them porous. Cowles emphasizes the fact that the rapidity of the conversion is dependent upon the amount of surface exposed to the salt and steam. It is stated that the reaction is rapid at 1800°F. The principal products of the reaction are sodium silicoaluminate and hydrochloric acid. Considerable work has been done on this process on a semi-commercial scale at Sewaren, N. J.[2] Hall[3] heats briquets of aluminous material (high in silica) and sodium chloride to a temperature of 1600 to 1700°F. for 4 hours in the presence of steam. The resulting sodium aluminum silicate is ground and mixed with lime and soda and heated to 1300 to 1400°F. for 2 to 3 hours. A sinter is formed which is ground and leached with water to dissolve sodium aluminate. Separation of the silica and alumina in this process would be difficult and incomplete.

Processes of Extracting Alumina from Cryolite.

At the present time cryolite is seldom if ever used for the production of alumina. At one time it was used for the production of soda, since cryolite and calcium hydrate react to form insoluble calcium fluoride and soluble sodium aluminate. The alumina is a by-product when the sodium aluminate solution is decomposed with carbon dioxide. It is stated by Hagemann[4] that soluble aluminate is formed when a mixture of cryolite, lime, and bauxite is calcined at a red heat. Loewig and Loewig[5] add enough bauxite to the cryolite and lime mixture before heating so as to form the normal aluminate. ($1Al_2O_3$ to $1Na_2O$).

[1] Cowles, A. H., U. S. Pats. 1,040,893, 1,040,894, 1,040,977, Oct. 8, 1912; 1,041,598, 1,041,599, Oct. 15, 1912; 1,111,881, Sept. 29, 1914; 1,123,693, Jan. 5, 1915; Br. Pats. 19,605 (1912); 19,604 (1912), Feb. 20, 1913; Fr. Pats. 448,165, 448,166, Jan. 24, 1913; Norw. Pat. 26.706, Feb. 28, 1916.

[2] Cowles, A. H., *Met. Chem. Eng.*, **10**, 659 (1912).
　Proc. 8th Int. Cong. App. Chem., *Met. Chem. Eng.* **11**, 140 (1913).
　J. Ind. Eng. Chem. **5**, 331 (1913).
　Eng. Mining. J. **94**, 536 (1912).

[3] Hall, C. M., U. S. Pat. 1,282,222, Oct. 22, 1918.

[4] Hagemann, G. A., U. S. Pat. 87,042, Feb. 16, 1869.

[5] Loewig, F. and G. Loewig, Br. Pat. 1,556 (1877) Sept. 15, 1877.

Petraeus[1] roasts the cryolite and caustic lime and then leaches with water. This solution is boiled with bauxite to dissolve the alumina. It is also stated that alumina is dissolved when a mixture of bauxite and cryolite is boiled with a solution of caustic lime. Bauer[2] obtains a mixture of alumina and calcium fluoride by digesting 1 part cryolite, 1 part calcium carbonate, 30 to 40 parts water, and 1 per cent alkali carbonate. Doremus[3] obtains the fluorine in the form of hydrofluoric acid by passing steam over cryolite heated just below its melting point. Silicon fluoride is also evolved while soluble sodium aluminate remains as a residue.

Processes of Extracting Alumina from Phosphates.

According to Prentice,[4] an aluminum phosphate ore is decomposed by fusing with sodium sulfate and carbon or by boiling with a solution of sodium carbonate or hydrate. The sodium phosphate may be crystallized out of the sodium aluminate solution and the alumina precipitated with carbon dioxide or calcium oxide.

It has been stated that the alumina may be obtained from natural aluminous phosphates[5] by digesting with sodium or potassium hydroxide. The alumina is to be precipitated from the alkali aluminate after the alkali phosphate has been removed by crystallization. Another method is suggested in which the phosphate is digested with lime and the alumina dissolved by means of sodium carbonate solution. Laboratory tests indicate that these separations are incomplete and unsatisfactory. Similar processes have been recently proposed and unsuccessfully tried in Japan by Onoda[6] who treats an aluminum phosphate ore with a mixture of sodium and calcium hydrates under a pressure of 3 to 6 atmospheres. Enough calcium hydrate is used to combine with both the phosphoric acid and the silica, the calcium salts of which are insoluble (?) and, therefore, easily removed from the soluble alkali aluminate. Perry[7] first calcines the aluminum phosphate ore and then boils with sodium hydroxide solution. The sodium phosphate and aluminate are both soluble and must be separated. The aluminum can be precipitated by heating with silica under pressure or by treating with sodium silicate.

Robinson[8] uses a mixture of sodium hydroxide and sodium sulfide to decompose the aluminum phosphate ore. The iron oxide and

[1] PETRAEUS, C. V., U. S. Pats. 222,152, 222,153, 222,154, Dec. 2, 1879.

[2] BAUER, H., Ger. Pat. 54,824, Dec. 4, 1890.

[3] DOREMUS, C. A., U. S. Pat. 660,094, Oct. 23, 1900; Br. Pat. 18,969 (1900) May 4, 1901; Ger. Pat. 139,626, Feb. 27, 1903.

[4] PRENTICE, M., Br. Pat. 1,178 (1875) Nov. 2, 1875.

[5] TOWNSEND, J., Br. Pat. 995 (1871) applied for Apr. 14, 1871.

[6] ONODA, T., Jap. Pat. 63,082, Mar. 31, 1925.

[7] PERRY, D., Br. Pat. 156 (1882) applied for July 11, 1882.

[8] ROBINSON, W. E., Br. Pat. 2,069 (1876) applied for May 16, 1876.

sulfide are filtered off, the sodium phosphate recovered by crystallization, and the alumina precipitated from the sodium aluminate. In the patent to Humfrey,[1] the phosphate ore is first calcined and then ground and mixed with caustic soda solution and sufficient sodium silicate to combine with all the alumina The mixture is allowed to stand 24 hours and then lixiviated with hot water to dissolve out the soluble phosphate. The insoluble sodium silico-aluminate is ground in a mortar with lime to recover soda! It is stated that alumina may be used to combine with the phosphorus in the iron ore used in the blast furnace.[2] The resulting aluminum phosphate is heated with salt and carbon in the presence of steam to form soluble sodium aluminate and phosphate. It is doubtful whether even the first part of this process can be made to take place, since practical experience in smelting ores with high alumina slags (see Joseph, Kinney, and Wood, p. 144) did not show a removal of phosphorus in the slag. Tilghman[3] heats alumina or subphosphate of aluminum to a red heat with alkali sulfate or chloride in a current of steam and obtains soluble alkali aluminate. To obtain the phosphorus as the oxide, Peacock[4] heats a mixture of alumina and calcium phosphate in thin layers to form calcium aluminate and volatile phosphorus pentoxide. In a process for the production of phosphorus, Collet[5] adds 10 parts bauxite to a mixture of 15 parts raw calcium phosphate, 3 parts coal and 1 part sodium carbonate, and heats in the electric furnace to liberate the elementary phosphorus as a gas. The calcium aluminate slag may be decomposed with sodium carbonate solution to give soluble sodium aluminate from which pure alumina may be obtained. A recent British patent[6] states that an aluminum phosphate ore is decomposed by heating with alkaline earth compounds and alkali salts. The resulting alkali aluminate is soluble in water, while the alkaline earth phosphate is insoluble. The addition of sulfides or chlorides in the presence of steam is said to speed up the reaction.

Desilication and Special Treatment of Aluminate Solutions.

In connection with the various processes for the formation of soluble aluminates, no general discussion has been given of the removal of silica and other impurities and the precipitation

[1] Humfrey, C., Br. Pat. 3,323 (1877) Feb. 28, 1878.

[2] Twynam, T., Br. Pat. 5,386 (1888) Mar. 16, 1889.

[3] Tilghman, R. A., U. S. Pat. 5,383, Dec. 4, 1847.

[4] Peacock, S., U. S. Pat. 1,000,290, Aug. 8, 1911.

[5] Collet, E., Norw. Pat. 41,453, June 15, 1925.

[6] Rhenania Kunheim Verein Chemischer Fabriken A.-G., Br Pat. 283,072, Jan. 5, 1928.

of the alumina.   In any digestion of aluminous material with alkali, most of the silica present is attacked by the solution. Probably all of the silica in the form of clay and perhaps some of it which may be present in the form of sand, goes into solution, but is reprecipitated again as insoluble sodium aluminum silicate.   Some of the silica may be retained, however, in soluble form in the sodium aluminate solution, particularly where concentrated solutions of alkali are employed for digestion. Where appreciable quantities of silica are thus retained in solution, it is usually desirable to subject the solution to some treatment to remove as much of the silica as possible before proceeding with the precipitation of the alumina.

The formation of an insoluble sodium aluminum silicate going into the red mud is mentioned by Bayer and Le Chatelier. Hall[1] adds lime directly to the digester to causticize sodium carbonate (convert it to sodium hydroxide) and also to prevent the solution of silica.   The early patents to Loewig[2] describe various methods for the purification of alumina used in the sugar refineries and other industries which require adsorptive alumina. Caustic lime is said to remove iron and titanium oxides and silica from aluminate solutions.   Experience shows, however, that an excess of it may also precipitate alumina.   Le Chatelier[3] treats the alkali aluminate solution with acetic acid to precipitate the silica and leave soluble acetates of sodium and aluminum in solution.   The sodium is then precipitated by adding fluosilicate of aluminum.   If hydrochloric acid is used in place of acetic, the sodium is preferably precipitated with hydrofluosilicic acid. Neither scheme seems practical.

A French patent[4] states that the silica is precipitated from a sodium aluminate solution by merely digesting it at a pressure of 6 kilograms for $2\frac{1}{2}$ to 3 hours.   A later patent[5] by the same company adds that the longer the solution is digested and the higher the pressure, the less silica remains in solution.   Metzker

[1] HALL, C. M., U. S. Pat. 663,167, Dec. 4, 1900; Br. Pat. 14,573 (1900) June 29, 1901; Ger. Pat. 138,219, Jan. 3, 1903.

[2] LOEWIG, F., Br. Pat. 3,195 (1879) Oct. 21, 1879; Ger. Pat. 6,713, Oct. 13, 1878.

[3] LE CHATELIER, Br. Pat. 1,988 (1858) applied for Mar. 1, 1859.

[4] COMPAGNIE DES PRODUITS CHIMIQUES D'ALAIS ET DE LA CAMARGUE, Fr. Pat. 339,049, Oct. 20, 1904; Br. Pat. 19,924 (1904) Oct. 20, 1904.

[5] COMPAGNIE DES PRODUITS CHIMIQUES D'ALAIS ET DE LA CAMARGUE, Ger. Pat. 197,881, May 2, 1908.

and Russ[1] have described the results of tests of this method of desilication. Sherwin[2] also states that the silica may be removed from the aluminate solution by digesting at temperatures of about 290°F. under pressure. Practical experience substantiates these statements.

Vergé[3] increases the soda ratio before he removes the silica by a pressure digest. McCulloch[4] first precipitates the alumina and some silica by means of carbon dioxide and then redissolves the silica by adding fresh sodium hydroxide (equivalent to about 10 per cent of the total soda present calculated as sodium hydroxide) and digesting under pressure for 1 to 3 hours. Very little alumina goes into solution while practically all of the silica is redissolved. Practically the same results are claimed to be obtained if the precipitation with carbon dioxide is stopped before all of the alumina is precipitated.[5] Most of the silica remains in solution. Martin[6] avoids the solution of silica by digesting the calcium aluminate with a sodium carbonate solution partly saturated with aluminate. Arsandaux[7] adds sodium carbonate and an equivalent amount of calcium hydrate to the aluminate solution. The precipitated calcium carbonate carries down the silica. The addition of freshly precipitated calcium carbonate[8] to the aluminate solution which is subjected to a pressure of 2 to 3 atmospheres for 1 to 2 hours is said to remove the silica. It is understood that this process has had extensive commercial use. Peniakoff[9] claims that less pressure and time are required if calcium aluminate is substituted for

[1] METZKER, R. and F. RUSS *Chem. tech. Mitt. Staatsgewerbeschule,* Wien, **17**, 1 (1912).

[2] SHERWIN, R. S., U. S. Pat. 1,422,004, July 4, 1922.

VERGÉ, A., Fr. Pat. 373,070, Apr. 30, 1907.

[4] McCULLOCH, G., U. S. Pat. 938,269, Oct. 26, 1909.

[5] McCULLOCH, G., U. S. Pat. 941,799, Nov. 30, 1909.

[6] MARTIN, E., U. S. Pat. 1,394,854, Oct. 25, 1921; Br. Pat. 9,662 (1915) Nov. 18, 1915; Fr. Pat. 475,476, May 18, 1915; Ger. Pat. 332,389, Feb. 3, 1921; Swed. Pat. 47,962, June 30, 1919; Swiss Pat. 89,956, July 16, 1921; Norw. Pat. 33,535, Nov. 14, 1921.

[7] ARSANDAUX, H., Fr. Pat. 361, 766, Oct. 31, 1906; Add. Pat. 7,843, Oct. 30, 1907.

[8] COMPAGNIE DES PRODUITS CHIMIQUES D'ALAIS ET DE LA CAMARGUE, Br. Pat. 27,290 (1906) Jan. 24, 1907.

[9] PENIAKOFF, D. A., Br. Pat. 17,356 (1908) Aug. 5, 1909; Ger. Pat. 221,376, Apr. 25, 1910; Norw. Pat. 18,901, July 15, 1908; Fr. Pat. 392,187, Nov. 19, 1908; Swed. Pat. 27,290, Aug. 7, 1909.

the carbonate. Any excess of calcium aluminate may be decomposed with sodium carbonate.

Peffer[1] claims that the silica content of the solution obtained by digesting bauxite with sodium hydrate is reduced if it is allowed to stand quietly in contact with the red mud for several hours. On the other hand, Howard,[2] after diluting the solution, heats it to 100°C. with live steam in the presence of the red mud and prefers agitation.

Hulin[3] proposes to treat the aluminate solution with barium hydrate or aluminate, since the barium salts of silicic, phosphoric, titanic, ferric, and chromic acids are insoluble and precipitate. Hand and Kunheim[4] make the improbable statement that the addition of a small amount of phosphate either to the bauxite and soda fusion mixture or to the aluminate solution itself will make the silica insoluble. The phosphoric acid is to be precipitated from the solution with a little lime and this brings down the last of the silica.

Vergé[5] adds the bauxite directly to a special digester which disintegrates the solid in situ by very rapid stirring in the sodium hydroxide solution and then digests the mixture at 2.5 to 3 atmospheres pressure while the agitation is continued. The patent states that very little silica is found in the final product since the temperature employed is low, and, therefore, ores containing higher percentages of silica may be used.

Spence and Craig[6] state that alumina does not spontaneously precipitate from a sodium aluminate solution which is stabilized by the addition of 1 to $1\frac{1}{2}$ per cent of sugar, glycerine, or starch. Some organic matter is usually found in the raw material as humus, etc., and its presence in the aluminate solution may be an objectionable feature, especially in the auto-precipitation process if alumina is actually held up by the presence of organic matter. This is a debatable question and can not be answered at the present time. A calcination of the crude material will

[1] Peffer, H. C., U. S. Pat. 938,432, Oct. 26, 1909.

[2] Howard, H., U. S. Pat. 1,137,860, May 4, 1915.

[3] Hulin, P. L., Ger. Pat. 71,407, Oct. 2, 1893.

[4] Hand, A. and H. Kunheim, Br. Pat. 14,657 (1892) June 10, 1893; Ger. Pat. 68,394, Apr. 10, 1893.

[5] Vergé, A., Fr. Pat. 397,211, May 3, 1909.

[6] Spence, H. and T. J. I. Craig, U. S. Pat. 1,157,436, Oct. 19, 1915; Br. Pat. 20,970 (1913) Sept. 17, 1914.

destroy the organic matter. Bleaching powder[1] or sodium hypochlorite[2] have also been proposed as a means of destroying the organic matter in the original material. Hirsch and Russ[3] pass ozone through a dark-colored solution of sodium aluminate to destroy the organic matter and claim a more complete precipitation of alumina which is pure white.

Precipitation of Alumina from Aluminate Solutions.

A very early English patent by Le Chatelier[4] lists the various means which may be used to precipitate alumina from an aluminate solution.

1. Carbon dioxide gas.
2. Sodium bicarbonate.
3. Ammonium carbonate and bicarbonate.
4. Spontaneous separation of alumina from an aluminate solution supersaturated with alumina.
5. Acids, especially hydrochloric, hydrogen sulfide being also mentioned.
6. Ammonium chloride, calcium chloride, etc.
7. Aluminum chloride solution.
8. Metallic salts, especially chlorides. (Metallic base and alumina precipitated.)

Bayer[5] precipitates the alumina by agitating the solution with a seed charge of aluminum hydrate. Instead of rapidly agitating the solution, Fickes[6] proposes to pump the solution and the suspended hydrate from the bottom to the top of the tank and allow the alumina slowly to settle through the solution. Sherwin[7] varies the procedure somewhat, since, after pumping the material from the bottom, it is sprayed through the air (to

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[1] BRADBURN, J. A. and J. D. PENNOCK, U. S. Pat. 461,416, Oct. 20, 1891; Br. Pat. 17,933 (1891) Nov. 28, 1891.

[2] KLEINMANN, F., Br. Pat. 266,225, Feb. 25, 1927; Fr. Pat. 575,790, Aug. 6, 1924; Ger. Pat. 439,540, Jan. 15, 1927.

[3] HIRSCH, F. and F. RUSS, Ger. Pat. 284,601, June 2, 1915

[4] LE CHATELIER, Br. Pat. 957 (1859) Sept. 29, 1859.

[5] BAYER, K. J., U. S. Pat. 382,505, May 8, 1888; Ger. Pat. 43,977, Aug. 3, 1888; Br. Pat. 10,093 (1887) June 15, 1888. For a continuous process see COMPAGNIE DES PRODUITS CHIMIQUES ET ÉLECTROMÉTALLURGIQUE ALAIS, FROGES, ET CAMARGUE, Fr. Pat., 614,863, Dec. 24, 1926.

[6] FICKES, E. S., U. S. Pat. Reissue 13,668, Jan. 6, 1914; Br. Pat. 26,903 (1912) May 8, 1913; Fr. Pat. 451,593, Apr. 22, 1913; Ger. Pat. 311,368, Mar. 20, 1919.

[7] SHERWIN, R. S., U. S. Pats. 1,251,295, 1,251,296, Dec. 25, 1917

cool), into the top of the tank. Both procedures have been extensively used commercially.

Starting with an aluminate solution of 50° Bé. gravity, Teteléni[1] dilutes it with 5 to 6 volumes cold water in order to precipitate the alumina. It is preferable to add the water in several portions and filter after each dilution.

Alumina may be precipitated from a concentrated barium aluminate solution by agitation, preferably in the presence of crystallized alumina, or the barium may be first eliminated as insoluble barium sulfate by adding sodium sulfate and the soluble sodium aluminate treated in the regular manner.[2]

Russ[3] investigated the conditions favorable to the precipitation of alumina in the Bayer process and recommended having the alumina and soda present in the molecular proportions of $1 Al_2O_3$ to $1.24 Na_2O$ in a solution of specific gravity 1.24; under these conditions, a yield of 85 per cent of the alumina present is obtained.

Alumina is precipitated from an alkali aluminate solution by carbon dioxide. The conditions of the precipitation may be varied to take care of certain impurities. Jordan[4] preheats the carbon dioxide between 200 and 400°F. before passing it into the solution. This heating is claimed to prevent the formation of insoluble sodium compounds, and hence the soda content of the alumina is reduced. Miner[5] precipitates the alumina from an aluminate solution by means of carbon dioxide at a temperature high enough to keep the silica in solution. Peniakoff[6] proposes to purify the carbonate after the alumina is filtered off by passing in more carbon dioxide to precipitate the bicarbonate, which is insoluble and can be removed by filtration.

It is claimed that an insoluble compound of sodium and aluminum may be made by adding an aluminate solution to a sodium bicarbonate solution saturated with carbon dioxide. This "carbonated alkali aluminate"[7] $Na_2O.Al_2O_3.2CO_2.5H_2O$,

[1] TETELÉNI, A. and I. SZIRMAY, Ger. Pats. 299,652, 299,653, Oct. 4, 1919; Swiss Pat. 73,101, Aug. 16, 1916.

[2] PENIAKOFF, D. A., Br. Pats. 6,096 (1896) applied for Nov. 19, 1896; 10,252 (1896) applied for May 13, 1896.

[3] RUSS, F., Z. anorg. Chem., **41**, 216 (1904).

[4] JORDAN, H. W., U. S. Pat. 691,470, Jan. 21, 1902.

[5] MINER, C. G., U. S. Pat. 1,324,318, Dec. 9, 1919.

[6] PENIAKOFF, D. A., Fr. Pat. 405,611, Jan. 8, 1910.

[7] LOEWIG, F., Br. Pat. 3,195 (1879) Oct. 21, 1879; Ger. Pats. 6,713, Oct. 13, 1878; 19,784, Oct. 12, 1882.

is soluble in dilute acids. The addition of a saturated solution of sodium bicarbonate to a solution of sodium aluminate is said to precipitate a carbonated compound whose formula is $3Na_2O.-3Al_2O_3.5CO_2$. When magnesium bicarbonate is substituted for the alkali bicarbonate, a similar compound, $Al_2O_3.MgCO_3.3H_2O$, is precipitated.[1] Nishiri[2] recommends the addition of minute quantities (0.01 per cent) of ammonium salts, such as ammonium carbonate, to aid in precipitation.

While carbon dioxide is more commonly used, several investigators have suggested the use of hydrogen sulfide[3] or sulfur dioxide[4] as a means of precipitating alumina from aluminate solutions. If it were not so expensive and poisonous, hydrogen sulfide could be used to advantage in the case of a barium aluminate solution, since barium carbonate is insoluble and barium sulfide is soluble.

It is stated that alumina may be prepared from calcium aluminate[5] by cautiously adding hydrochloric acid and dissolving out the soluble calcium chloride. Another method[6] consists in dissolving some aluminate completely in hydrochloric acid and then adding an equivalent quantity of aluminate, whereby the alumina is precipitated. A solution of aluminum chloride[7] also may be added to an aluminate solution to precipitate the alumina.

Roberts[8] and Schwerin[9] have proposed electrolytic methods of separating alumina from aluminate solutions; they appear expensive and impractical.

[1] LOEWIG, F., Ger. Pat. 70,175, July 5, 1893.

[2] NISHIRI, T., Jap. Pat. 36,046, Mar. 29, 1920.

[3] MÜLLER, H., Ger. Pat. 230,118, Jan. 16, 1911; PERNOT, L. and J. GUIRARD, Fr. Pat. 405,891, Jan. 15, 1910; LE CHATELIER, Br. Pat. 957 (1859) Sept. 29, 1859.

[4] CLEMM, A., U. S. Pats. 845,854, Mar. 5, 1907; 848,612, Mar. 26, 1907; Br. Pat. 5,478 (1906) Mar. 6, 1907; Ger. Pats. 180,554, Jan. 24,1907; 185,030, May 14, 1907; Fr. Pat. 363,893, Aug. 9, 1906.

[5] LOEWIG, F., and G. LOEWIG, Br. Pat. 1,556 (1877) Sept. 15, 1877.

[6] LOEWIG, G., U. S. Pat. 201,028, Mar. 5, 1878; Ger. Pats. 93, July 3, 1877; 1,650, Dec. 21, 1877; 2,248, Feb. 5, 1878; DUTT, E. E., U. S. Pat. 1,332,115, Feb. 24, 1920; Br. Pat. 120,838, Nov. 28, 1918.

[7] SIMON, A., and L. PERNOT, Fr. Pat. 405,135, Dec. 20, 1909.

[8] ROBERTS, I. L., U. S. Pat. 683,000, Sept. 17, 1901.

[9] SCHWERIN, B., U. S. Pat. 1,216,371, Feb. 20, 1917; Br. Pats. 6,727 (1915) July 22, 1915; 7,212 (1915) Sept. 16, 1915; Fr. Pat. 511, 712, Jan.3, 1921; Ger. Pat. 305,364, Apr. 30, 1918; Swiss Pat. 71,918, Mar. 1, 1916.

Alumina precipitated by carbon dioxide may contain some insoluble sodium compound. This soda may be removed[1] by boiling the alumina with a solution of ammonium salt, such as ammonium chloride. Ammonia and soluble sodium chloride are formed. According to Peacock,[2] the last traces of alkali in crude alumina may be removed by digesting with silica and steam under pressure to form soluble alkali silicate.

Sherwin[3] has patented the use of a thickener and classifier of the Dorr type for the removal of the aluminum hydrate from the mother liquor and the separation of the coarse and fine particles.

ALUMINA AND THE CRYSTALLINE HYDRATES OF ALUMINUM

The hydrated oxides of aluminum have been the subject of a large number of investigations because of their interesting properties, and many attempts have been made to determine their composition and constitution. This has led to conflicting statements in the literature, and it has been only since the application of X-ray methods to the problem that the different compounds have been accurately classified. There now have been identified two hydrates, the monohydrate and the trihydrate, in addition to the anhydrous oxide. Two or more crystalline forms of each have been discovered, however, and something learned of the conditions under which each is formed. In order to identify each form, the following nomenclature for the different forms of alumina (Al_2O_3) is in use and a similar nomenclature is proposed for the hydrates of aluminum.

α-Al_2O_3 (corundum).

The oxide Al_2O_3 is found widespread in nature as the mineral corundum. α-alumina (artificial corundum) melts, according to Kanolt,[4] at 2050°C. According to Wright,[5] its refractive indices

[1] BRADBURN, J. A., and J. D. PENNOCK, U. S. Pat. 461,416, Oct. 20, 1891; SZIRMAY, I., and A. TETELÉNI, Ger. Pat. 299,653, Oct. 4, 1919; NORSK HYDRO-ELEKTRISK KVAELSTOF A/S, Fr. Pat. 579,864, Oct. 25, 1924.

[2] PEACOCK, S., U. S. Pats. 1,035,812, Aug. 13, 1912; 1,036,897, Aug. 27, 1912.

[3] SHERWIN, R. S., U. S. Pats. 1,315,045, 1,314,709, 1,314,710, Sept. 2, 1919; Br. Pat. 153,352, Nov. 11, 1920; Fr. Pat. 501,788, Apr. 23, 1920; Norw. Pat. 32,151, Apr. 18, 1921.

[4] KANOLT, J., Wash. Acad. Sci., 3, 315 (1913).

[5] WRIGHT, F. E., Am. J. Sci., 28, 321 (1909).

are $\epsilon = 1.760$ and $\omega = 1.768$, and its hardness 9, while its mean refractive index is 1.765, according to Rankin and Merwin.[1] Its density is 3.91. It is the form which fused alumina ordinarily takes upon solidification. The hydrates of aluminum are also converted to α-alumina upon ignition at high temperatures, above about 1200°C., and slowly at even lower temperatures. The crystal structure of α-alumina has been investigated by Davey and Hoffman,[2] Bragg and Bragg,[3] Davey,[4] Maginn,[5] Pauling and Hendricks,[6] and Ullrich.[7]

β-Al$_2$O$_3$.

Rankin and Merwin[8] have discovered another form of alumina, not found in nature, which they have designated as β-alumina. They have described it as follows:

β, the new form of alumina, is found to occur occasionally in charges of pure alumina which have been melted and slowly cooled. Having once formed, it has not been found possible to cause this form to revert to the α-form, even when held at temperatures above or below that required for melting. The presence of a small amount of MgO (0.5 per cent) materially assists in the formation of this new form, while melted alumina containing small amounts of either CaO or SiO$_2$ when cooled has been found to crystallize as the α-form (corundum). It would appear, therefore, that β-Al$_2$O$_3$ may be monotropic with respect to the α-form, although the exact relation existing between these two forms is uncertain by reason of the experimental difficulties involved in investigations requiring such extremely high temperature.

β-Al$_2$O$_3$ is hexagonal, often appearing in groups of overlapping triangular plates with perfect basal cleavage. The refractive index appears to vary, even in preparations made from our purest alumina, due account being taken of the difficulty of getting properly oriented sections. The values found are 1.635 to 1.650. In the same preparations, ω was 1.677 ± 0.003. In preparations containing MgO, ϵ may be as low as 1.629, and ω may vary between 1.665 and 1.680. But no relation between the content of MgO in the melt and the refractive index of the crystals has appeared.

[1] RANKIN, G. A., H. E. MERWIN, *J. Am. Chem. Soc.*, **38**, 568 (1916).

[2] DAVEY, W. P., E. O. HOFFMAN, *Phys. Rev.*, **15**, p. 333 (1920).

[3] BRAGG, W. H. and W. L. BRAGG, " X-ray and Crystal Structure," 3rd Ed.

[4] DAVEY, W. P., *Phys. Rev.*, **21**, 716 (1923).

[5] MAGINN, *Compt. rend.*, **178**, 785 (1924).

[6] PAULING, L. and S. B. HENDRICKS, *J. Am. Chem. Soc.*, **47**, 781 (1925).

[7] ULLRICH, *Norsk Geol. Tidskrift*, **8**, 115 (1925).

[8] RANKIN, G. A., H. E. MERWIN, *J. Am. Chem. Soc.*, **38**, 568 (1916).

Some artificial alumina[1] abrasives have been found to contain small amounts of this, β-Al_2O_3 having $\epsilon = 1.631$ and $\omega = 1.674$.

Saunders and White have patented a method of producing β-Al_2O_3 by fusing alumina with a sodium compound such as sodium carbonate.[2]   Ullrich,[3] Pauling and Björkeson,[4] and Gottfried[5] have investigated the crystal structure of β-Al_2O_3.

γ-Al_2O_3.

When aluminum monohydrate or trihydrate are dehyrated by heating, the product first formed is amorphous.   When the heating is continued at higher temperatures, say above 500°C., a new phase begins to appear which gives an X-ray pattern different from that of the hydrates or alumina.   This transition phase may be designated as γ-alumina.   Heating γ-alumina at temperatures above about 1200°C. results in its conversion to α-alumina; the lines of corundum appear faintly on long heating at somewhat lower temperatures.   It appears to be the same product listed by Hansen and Brownmiller[6] as γ-alumina and formed by heating precipitated alumina for 6 hours at 900 to 950°C.   Describing it, they state:

Microscopic examination showed this material to be isotropic with an index of refraction of 1.696 ± 0.003. Its specific gravity was found to be 3.47.   This probably is the same as the material reported by Ullrich[7] as γ-alumina.   Its X-ray diffraction pattern does not correspond to that of the β-alumina described by Rankin and Merwin.

α-Al_2O_3.$3H_2O$ (gibbsite).

Aluminum trihydrate occurs in nature as the mineral gibbsite, and this form of trihydrate is found in the so-called "trihydrate bauxites."   It can be made by auto-precipitation from sodium aluminate solutions, as in the Bayer process.   Milligan,[8] in the authors' laboratory, has shown that auto-precipitated aluminum

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[1] β-Al_2O_3 separated from artificial alumina abrasive was analyzed by H. S. Washington and found to have the chemical composition Al_2O_3; its density is 3.30 ± 0.01.

[2] SAUNDERS, L. E., and R. H. WHITE, U. S. Pat. 1,263,708, April 23, 1918.

[3] ULLRICH, *Norsk Geol. Tidskrift* **8**, 115 (1925).

[4] PAULING, L., A. BJÖRKESON, *Proc. Nat. Acad. Sci.*, **11**, 445 (1925).

[5] GOTTFRIED, C., *Z. Kryst*, **66**, 393 (1928).

[6] HANSEN, W. C., L. T. BROWNMILLER, *Am. J. Sci.*, V, **15**, 225 (1928). See also DE LAPPARENT, J., E. STEMPFEL, *Compt. rend.*, **187**, 305 (1928).

[7] ULLRICH, *Norsk. Geol. Tidskrift*, **8**, 115 (1925).

[8] MILLIGAN, L., *J. Phys. Chem.*, **26**, 247 (1922).

trihydrate, made in the commercial operation of the Bayer process, gives the same X-ray pattern as gibbsite. Gibbsite is monoclinic and its refractive indices are $\alpha = 1.566$, $\beta = 1.566$, $\gamma = 1.587$.[1]

β-Al$_2$O$_3$.3H$_2$O.

Böhm,[2] Hansen and Brownmiller,[3] Huttig and von Witt-genstein,[4] Biltz, Meisel, and Lehrer,[5] and Fricke,[6] as well as the senior author, have observed the fact that the trihydrate pre-cipitated under certain conditions gives a different X-ray pattern and has different properties from α-trihydrate or gibbsite. This form, which may be designated as β-Al$_2$O$_3$.3H$_2$O or simply β-trihydrate, is produced by precipitating aluminum chloride solutions with ammonium hydroxide in the cold, by saturating a solution of sodium aluminate with carbon dioxide, or even by auto-precipitation from sodium aluminate solutions under certain conditions. It can be dried at 110°C. without loss of water or change of form. It is more soluble in alkali than the α-trihydrate and appears to be a metastable phase, since it goes over to α-trihydrate upon continued shaking or long standing in contact with alkali. The transformation to α-trihydrate is accelerated by heating in contact with alkali solution. Fricke states that the formation of β-trihydrate occurs when the precipitation is comparatively rapid, and that with *very, very* slow precipitation, α-trihydrate is formed.

Biltz, Meisel, and Lehrer express the opinion that β-trihydrate is a hydrate of the monohydrate and give it the formula (Al$_2$O$_3$. H$_2$O).2H$_2$O, while Huttig and von Wittgenstein call it an "isomer" of gibbsite.

Experiments in the authors' laboratory have shown that alumina, auto-precipitated in test tubes, and which has stood in contact with sodium hydroxide solution for 20 hours at room temperature, is β-trihydrate. After standing in contact with

[1] Larsen, E. S., *U. S. Geol. Survey Bull.* **679**, 213 (1921).

[2] Böhm, J., *Z. anorg. allgem. Chem.*, **149**, 203 (1925).

[3] Hansen, W. C., L. T. Brownmiller, *Am. J. Sci.*, **5**, No. 15, 229 (1928).

[4] Huttig, G. F., E. von Wittgenstein, *Z. anorg. allgem. Chem.*, **171**, 323 (1928).

[5] Biltz, W., K. Meisel, G. A. Lehrer, *Z. anorg. allgem. Chem.*, **172**, 292 (1928).

[6] Fricke, R., *Z. anorg. allgem. Chem.*, **175**, 249 (1928).

alkali for ten days, the X-ray pattern has begun to show signs of a new phase; after 7 months, it gives the pattern for α-trihydrate. Aluminum trihydrate precipitated from alkali solution with carbon dioxide gives the β-trihydrate pattern, but after boiling in sodium hydroxide (110°C.) for 24 hours, it was partially converted to α-trihydrate. These experiments are in agreement with the findings of Fricke. On the basis of his laboratory experiments, which showed β-trihydrate formed by auto-precipitation from sodium aluminate solutions (even when seeded with α-trihydrate), Fricke concluded that it was the form obtained in the Bayer process and suggested calling it "bayerite." This conclusion was incorrect, however, for, as noted by Milligan and checked many times by us, the Bayer process (auto-precipitation without carbonation) operated on a large scale yields α-trihydrate. Fricke later reached the same conclusion.[1]

α-Al$_2$O$_3$.H$_2$O.

Aluminum monohydrate is a common constituent of many bauxites, of which French bauxites are typical. The name α-monohydrate is suggested for this form of monohydrate. The formation of α-monohydrate by heating α-trihydrate in alkali (or water) under pressure was discovered by Tosterud,[2] although not published at the time, as it was the basis of pending patent applications.

Although appearing much later, Böhm[3] appears to have been the first to publish a description of the production of α-monohydrate, or "synthetic bauxite," as he called it.

β-Al$_2$O$_3$.H$_2$O (diaspore).

Another monohydrate of aluminum is found in nature as the mineral diaspore. Its X-ray pattern is characteristically different from that of α-monohydrate just described, and may be termed "β-monohydrate." The difference between the form of monohydrate found in bauxite and diaspore has also been noted by Haber,[4] Böhm,[5] and others. Diaspore is orthorhombic and its refractive indices are $\alpha = 1.702$, $\beta = 1.722$, $\gamma = 1.750$.[6]

[1] Fricke, R., *Z. anorg. allgem. Chem.*, **179**, 287 (1929).

[2] Tosterud, M., Can. Pat. 285,147, Nov. 27, 1928.

[3] Böhm, J., *Z. anorg. allgem. Chem.*, **149**, 203 (1925).

[4] Haber, F., *Naturw.*, **13**, 1007 (1925).

[5] Böhm, J., *Z. anorg. allgem. Chem.*, **149**, 203 (1925).

[6] Larsen, E. S., *U. S. Geol. Survey, Bull.*, **679**, 227 (1921).

Miscellaneous Uses of Alumina and Aluminum Hydrates.

Aside from its major use in the production of aluminum, the pure calcined alumina of the Bayer process has few uses except in the production of abrasives. Substantially pure fused alumina made in the electric furnace has extensive use as an abrasive and a more limited use in refractories made to withstand high temperatures.

Aluminum trihydrate is employed in relatively small quantities in the production of pure aluminum sulphate, sodium aluminate, hydrated aluminum chloride, and other pure salts of aluminum. It is also employed to some extent in the production of special glasses. After calcination at low temperatures, 400 to 600°C., it makes an excellent absorbing medium for water vapor and acts as a catalyst for several important reactions. The α-mono-hydrate made by Tosterud's[1] process may be produced in the form of an extremely light and fluffy powder with very low thermal conductivity. Ordinary calcined alumina weighs about 60 pounds per cubic foot, while the monohydrate can be made with a weight of only 20 to 30 pounds per cubic foot. As a loose powder and in various compounded forms, it makes an excellent thermal insulator capable of standing relatively high temperatures without substantial loss of insulating properties. The monohydrate in this form is very finely divided and has a soft, talc-like texture.

[1] *Loc. cit*

CHAPTER VI

ACID PROCESSES FOR THE EXTRACTION OF ALUMINA

By

FRANCIS C. FRARY AND RALPH B. MASON

As indicated in Chap. V, all of the commercially successful chemical processes for extracting alumina from its ores have so far been of the alkaline type. Many inventors have labored and much money has been spent on acid extraction processes, but to date no such process has gone into commercial production, although several have been carried to the semi-commercial stage of development. Their failure is generally due to their complicated nature, which makes it impossible for them to compete with the simple and cheap Bayer process.

Of their inherent difficulties, we have already mentioned, in Chap. V, the separation of iron from aluminum. The extent to which this separation would have to be carried is indicated by the fact that in order to get alumina equal to the commercial Bayer process grade (not over 0.05 per cent Fe_2O_3) by calcination of aluminum sulfate crystals, making no allowance for contamination during calcination, the original salt must contain less than 0.01 per cent ferric oxide. The difficulty of economically recovering substantially all of the acid reagent, to be used again in the process, is almost insurmountable, and serious losses not only raise costs rapidly, but also usually make trouble with the neighbors.

Whereas alkaline liquors can be handled and alkaline processes carried out in tanks, pumps, pipes, etc., of iron or steel, acid solutions require special, more expensive, and generally more fragile containers. Stoneware vessels, acid-proof brick tanks, lead-lined or rubber-lined equipment, special high-silicon "acid-proof" iron alloys, quartz tubes and dishes, and similar special equipment are easily handled in the laboratory but become very expensive in a commercial plant, where large volumes of dilute solutions must be carried through a complicated process to produce a relatively cheap but very pure substance.

Nevertheless, their ability to attack clay and other silicates has made the acid processes attractive to many inventors, and there yet may be found a combination of economic circumstances under which some such process may have a limited commercial use.

The search for a commercial process of extracting alumina from clay is frequently inspired by the thought that clay can be found anywhere and obtained at almost no cost. This, however, is an overly optimistic view of the situation. Clay contains, at best, but 30 to 40 per cent of alumina, and usually less, as compared with a 60 per cent alumina content for bauxite. Furthermore, the efficiency of alumina extraction is usually greater for bauxite than for clay.

Another reason for the interest in the utilization of clay for the production of alumina is that some countries which do not have adequate supplies of bauxite within their borders do have abundant clay deposits. In order to foster an aluminum industry, dependent for its raw supplies on domestic products, hundreds of possible processes for utilizing clay and ores other than bauxite have been investigated.

Because none of the so-called "acid processes" for the production of alumina have achieved any large commercial success, there is no single process which can be described as being typical in the way that the Bayer process is typical of the alkali digestion processes. In general, however, the acid processes involve the conversion of the aluminum compounds in the ore into aluminum salts, such as aluminum sulphate, chloride, or nitrate, and the purification of such salt. When the aluminum salt has been prepared in suitably pure form, the next problem is to convert it into aluminum oxide and recover the acid radical of the aluminum compound, either for use in the process or in some salable form.

A typical series of operations which might be used in the production of alumina from clay are as follows: The clay, which may or may not have undergone a roasting operation to make the alumina more readily soluble, is digested in an acid solution. The use of sulphuric acid for this operation has many advantages, in that sulphuric acid is cheaper than hydrochloric or nitric acid, and hence unavoidable losses do not place such a heavy charge on the process. The apparatus required for handling sulphuric acid is simpler and in general less expensive

than that required for handling nitric and hydrochloric acids. A solution containing about 60 per cent sulphuric acid seems

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┌─────────────────────────────┐      ┌─────────────────────────────┐
│ Preliminary treatment of ore│      │ Preliminary treatment of    │
│ to increase extraction of   │─────▶│ ore to remove iron as       │
│ alumina or decrease ex-     │      │ volatile or soluble compounds│
│ traction of impurities      │      │ and by magnetic separation  │
└─────────────────────────────┘      └─────────────────────────────┘
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| Treatment with acids such as sulfuric, nitric, hydrochloric, hydrofluoric | Treatment with salts especially acid salts | Treatment with acid gases |

Elimination of Iron
By precipitation of insoluble ferric compound, electrolysis or thermal decomposition, or
By crystallization of sulfate or alum, leaving iron in solution especially as chloride or as ferrous salt.

Production of alumina from purified salt

Precipitation of alumina by basic substances, leaving iron in solution as ferrous salt

Thermal process for decomposition of salt

Precipitation methods using sulfides, carbonates, hydrates, sulfites, lime, ammonia, sodium thiosulfate, iron, etc.

Recovery of acid radical

Aluminum hydrate (pure or with minor amounts of basic salts)

Alumina

FIG. 40.   Outline of unit operations in acid processes for producing alumina.

to be satisfactory for this purpose. The finely ground clay and acid solution are heated together with agitation until the maximum amount of alumina has been extracted. Depending

upon the clay used and other conditions, varying amounts of iron, silica, and titanium will have been extracted with the alumina, and the solution of aluminum sulphate will probably require further purification before a sufficiently pure aluminum sulphate can be prepared from it. A variety of procedures have been proposed for this purpose but none have been entirely satisfactory, partly because the iron in the product must be reduced to a very low figure. Alumina for the electrolytic reduction process should not contain more than about 0.05 per cent ferric oxide.

After purification, the solution is then concentrated by evaporation and the aluminum sulphate recovered in solid form. The next step might involve the drying of the aluminum sulphate preparatory to its calcination. The calcination process has for its object the decomposition of the aluminum sulphate into pure alumina and gaseous oxides of sulphur. The gaseous oxides of sulphur are then recovered in the form of sulphuric acid for use in the next cycle of the process. This is much easier said than done: the temperature required for complete decomposition of the sulphate is about 1000°C., and it is therefore difficult and expensive to calcine in any way except by direct heating, as in a rotary kiln. Such heating, however, involves mixing so much air and products of combustion with the sulfur dioxide, that the chamber or contact space required for the formation and condensation of the sulfuric acid becomes excessively large and expensive.

PRELIMINARY TREATMENT OF ORES

Roasting.

A survey of patent and technical literature shows that much work has been done on methods for increasing, by means of a suitable preliminary roast, the proportion of the alumina in aluminous ores (especially clays) extractable by acids. Heating may also decrease the solubility of the impurities, but the optimum temperature as regards the solubility of the alumina does not necessarily coincide with the optimum temperature for rendering the impurities insoluble. Also the conditions of roasting which produce satisfactory results with one ore are not necessarily the best conditions for another. It is usually necessary to determine the best treatment for every ore, and it is likely that

some of the apparent discrepancies in the patent literature refer to different materials and conditions.

Mellor and Scott[1] found that when kaolinite is heated, dehydration does not take place at a fixed temperature, but is completed above 500°C. At this temperature, it decomposes into free silica, alumina, and water; about 900°C. a further change occurs in the form of the alumina which renders it less soluble. Houldsworth and Cobb,[2] as well as Tammann and Pape,[3] have also made valuable observations along this line. Vesterberg,[4] Gerber,[5] and Sokolov[6] have investigated the increase in solubility of clay heated in the temperature range of about 400 to 900°C.

As examples of proposed preliminary treatments, the following may be cited: An English patent[7] states that leucite or similar aluminous ores should be heated first to 1100°C. before they are run into water or acid. The alkali and alumina remain soluble but the silica is insoluble. Lavoye[8] prefers to calcine clay at 600°C., while Richter and Richter[9] specify calcination in the absence of air. In order to obtain a more porous product to react with acid, Spence and Llewellyn[10] propose to mold clay into balls and calcine at a dull red heat. Yngström, Lindblad, and Bergschöld[11] fuse a natural alkali-aluminum silicate in the electric furnace, even reducing a part of the silica, as a preliminary step before treating it with an acid. Doremus[12] finds that a preliminary roasting of the ore at 540°C. makes it easier to dissolve the alumina in hydrofluoric acid, while Chappell[13]

[1] MELLOR, J. W., and A. SCOTT, *Trans. Ceram. Soc.* (England) **23**, 322 (1924).

[2] HOULDSWORTH, H. S., and J. W. COBB, *Trans. Ceram. Soc.* (England) **23**, 279 (1924).

[3] TAMMANN, G., and W. PAPE, *Z. anorg. allgem. Chem.*, **127**, 43 (1923)

[4] VESTERBERG, K. A., *Arkiv. Kemi. Mineral. Geol.*, **9**, No. 14 (1925).

[5] GERBER, V., *Z. Elektrochem.*, **25**, 193 (1919).

[6] SOKOLOV, A. M., *Tonind.-Ztg.*, **36**, 1107 (1912).

[7] RHENANIA VEREIN CHEMISCHER FABRIKEN A.-G., and H. BRENEK, Br. 218,998, Aug. 20, 1925.

[8] LAVOYE, M., Fr. Pat. 607,537, July 3, 1926.

[9] RICHTER and RICHTER, Ger. Pat. 244,538, Mar. 11, 1912.

[10] SPENCE, H. and W. B. LLEWELLYN, Br. Pat. 247,078, Feb. 8, 1926.

[11] YNGSTRÖM, L., A. R. LINDBLAD, and S. A. J. BERGSCHÖLD, Swed. Pats 40,757, June 7, 1916; 41,110, Aug. 9, 1916.

[12] DOREMUS, C. A., U. S. Pat. 1,391,172, Sept. 20, 1921; Fr. Pat. 506,392, Aug. 20, 1920.

[13] CHAPPELL, H. F., U. S. Pats. 1,079,899 and 1,079,900, Nov. 25, 1913.

states that alumina is rendered insoluble in hydrofluoric acid by heating to 1000 to 1500°C., while the silica remains soluble. A recent publication of the U. S. Bureau of Mines by Tilley, Millar, and Ralston[1] gives a summary of the literature dealing with the roasting of clays and other aluminous ores. After considering the results of previous workers and their own tests on the extraction of alumina and the various impurities in several typical ores which had been roasted at different temperatures, the authors conclude that the rate of extraction of alumina from clay is increased by calcination at temperatures of 500 to 900°C., and that roasting is desirable, in general.

Heating with Alkali or Alkaline Earth Compounds.

The literature contains many references to the use of a preliminary heating with alkali or alkaline earth compounds in order to facilitate the extraction of the alumina. In a number of these processes, the object is to convert part of the silica into a water-soluble alkali silicate which can be leached out, leaving the alumina in a form readily extracted by acids. With this idea in mind, Frazer, Holland, and Miller[2] propose to heat pulverized feldspar with caustic alkali for 2 hours at 185 to 350°C., and then leach out one-third of the silica as alkali silicate. The residue, which is similar to leucite in composition, is then decomposed with acid to recover potash and alumina. The original alkali may be obtained from the silicate solution with lime.

Muth[3] heats aluminum silicate or china clay to the boiling point with solutions of alkalies or alkaline earths and, after adding more alkali, heats under pressure to about 140°C. The soluble alkali silicate is leached out, leaving alumina to be recovered by some unnamed method. Wildman[4] states that clay is readily soluble in sulfurous acid if it is first boiled with alkali solution.

Morse[5] removes one-third of the silica by furnacing clay with caustic alkali at 300°C. and then extracting with water. Boehm[6] suggests mixing the clay with alkali solution in the form of a paste and then, by the passage of an electric current, evaporating the water and fusing

[1] TILLEY, G. S., R. W. MILLAR, O. C. RALSTON, *Bull.* **267**, 12, 14 (1926).

[2] FRAZER, J. C. W., W. W. HOLLAND, E. MILLER, U. S. Pat. 1,196,734, Aug. 29, 1916; see also *J. Ind. Eng. Chem.*, **9**, 935 (1917).

[3] MUTH, G., U. S. Pat. 1,527,903, Feb. 24, 1925; Br. Pat. 220,011, July 28, 1924.

[4] WILDMAN, H. G., U. S. Pat. 1,326,384, Dec. 30, 1919; Br. Pat. 161,310, Apr. 14, 1921; Fr. Pat. 509,142, Nov. 2, 1920.

[5] MORSE, H. N., U. S. Pat. 1,286,718, Dec. 3, 1918.

[6] BOEHM, W., Fr. Pat. 562,946, Nov. 22, 1923; Ger. Pat. 369,826, Jan. 16, 1924.

the mass, which is then poured into water to dissolve the alkali silicate. Stover[1] heats 1 part of orthoclase with 1½ parts of alkali metal carbonate, hydrate, or oxide to a red heat; carbon may be added to assist in the fusion. When the fused mass is run into water, the potassium compound dissolves, leaving suspended potassium-aluminum silicate which can be decomposed with acid. Ravner[2] uses material containing potash to decompose such substances as feldspar or leucite. The mixture is heated at 800 to 1000°C. and then leached with water to obtain the soluble potassium compounds. The alumina is dissolved in dilute acid. Scholes[3] furnaces equal parts of feldspar and sodium carbonate and then runs the fused mass into water. After pulverizing the material, it is digested with water for 2 hours under pressure at 160°C. The alkali silicate goes into solution, leaving insoluble alumina, etc., in the colloidal condition. A double silicate of aluminum and potassium which is acid soluble is prepared according to Swenarton[4] by heating potash feldspar with potassium carbonate at 800 to 1200°C. for ¾ to 1½ hours. By digesting with hot water and actively boiling, the potash dissolves, leaving the double silicate as a residue.

Another group of processes heats the aluminous mineral with alkali or alkaline earth compounds for the purpose of rendering the alumina more readily dissolved without reference to the silica. According to Le Verrier and Minet,[5] bauxite is made more soluble in acid by a preliminary heating with a small amount of sodium carbonate. Meyer[6] asserts that by heating clay to a red heat with alkali or alkaline earth chlorides, and especially aluminum chloride, the resulting mass is made more reactive towards acids. Peniakoff[7] furnaces clay with sodium sulfate and chloride and preferably with some sodium sulfide. In the presence of dry air, alumina, sodium silicate, and chlorine are formed. The claim is made that the sodium sulfate acts as a catalyst.

Lederer and Stanczak[8] heat clay in a digester with sodium carbonate solution under pressure and allow the mass to cool in an atmosphere of carbon dioxide. This treatment is supposed to leave the alumina in an acid-soluble condition while the silica remains insoluble.

[1] Stover, J. H., U. S. Pat. 1,283,951, Nov. 5, 1918.

[2] Ravner, O., Br. Pat. 102,493, Nov. 8, 1917; Norw. Pat. 27,039, June 26, 1916.

[3] Scholes, S. R., U. S. Pat. 1,312,053, Aug. 5, 1919.

[4] Swenarton, W. H., U. S. Pat. 1,277,773, Sept. 3, 1918.

[5] Le Verrier and Minet, Fr. Pat. 244,582, Jan. 24, 1895.

[6] Meyer, E., Br. Pat. 13,395 (1891) June 18, 1892.

[7] Peniakoff, D. A., Fr. Pat. 241,376.

[8] Lederer, O., and W. Stanczak, Br. Pat. 246,512, Oct. 14, 1926; Fr. Pat. 607,346, June 30, 1926; Swiss Pat. 122,586, Oct. 1, 1927; Czech. Pat. 18,648, May 25, 1926. See also Kassler, H., *Chem. Ztg.*, **50**, 917 (1926).

A Norwegian patent[1] states that an aluminous ore can be calcined at a low temperature with sodium sulfate and carbon without forming an aluminate and that the alumina in the ore so treated is then soluble in sulfurous acid. Hart[2] fuses feldspar with carbon and a sulfate of potassium, sodium, or barium, and then decomposes the resulting mass with sulfuric acid. Coolbaugh and Quinney[3] heat crushed kaolin with gypsum or limestone. The mass is quickly cooled, crushed, and leached with sulfuric acid.

Lindblad[4] fuses a mineral, such as nepheline syenite or leucite, with lime in a closed electric furnace before the material is extracted with acid.

McKee[5] furnaces a potash mica with limestone and salt with or without the addition of carbon and obtains the alumina from the water-insoluble residue by means of sulfuric acid. Eberhardt[6] calcines potash mica with fluorspar and gypsum before treating with sulfuric acid. Hepke[7] furnaces clay with magnesium sulfate and common salt at a temperature of 400 to 600°C. in the presence of air or steam. The products of the reaction are magnesium silicate, sodium sulfate alumina, and chlorine or hydrogen chloride. Foreign patents state[8] that a substance, such as feldspar, can be decomposed by heating with calcium cyanamide and carbon at a temperature of about 300°C. Upon treating the product with water vapor, ammonia is given off and the potassium and aluminum compounds can be extracted from the residue by means of water or acid, respectively.

Furnacing with Sulfur, Carbon, Steam, Etc.

A number of miscellaneous preliminary furnace treatments have been recommended. Raynaud[9] claims that furnacing the ore with a small quantity of sulfurous materials makes the alumina more soluble

[1] COMPAGNIE GÉNÉRALE L'ALUMINE SOCIÉTÉ ANONYME, Norw. Pat. 7,552, Sept. 4, 1899; Dan. Pat. 2,340, July 3, 1899.

[2] HART, E., U. S. Pats. 997,671, July 11, 1911; 1,062,278, May 20, 1913; *Proc. Eighth Intern. Congr. Appl. Chem.*, **2**, 117.

[3] COOLBAUGH, M. F., and E. H. QUINNEY, U. S. Pats. 1,170,418, Feb. 1, 1916; 1,178,384, Apr. 4, 1916; 1,125,007, Jan. 12, 1915; 1,165,154, Dec. 21, 1915.

[4] LINDBLAD, A. R., Swed. Pat. 41,783, Jan. 3, 1917.

[5] McKEE, R. H., U. S. Pat. 1,222,960, Apr. 17, 1917.

[6] EBERHARDT, L. A., U. S. Pat. 1,310,413, July 22, 1919.

[7] HEPKE, K., Ger. Pat. 427,806, Apr. 19, 1926.

[8] HALVORSEN, B. F., Norw. Pat. 27,453, Nov. 27, 1916. NORSK HYDRO-ELEKTRISK KVAEL, Fr. Pat. 500,825, Mar. 25, 1920.

[9] RAYNAUD, E., U. S. Pat. 650,763, May 29, 1900; Ger. Pat. 107,502, Nov. 14, 1899; Swed. Pat. 10,268, Oct. 14, 1899; Br. Pat. 22,265 (1898) Dec. 3, 1898.

in sulfurous acid. Rich[1] describes burning an aluminous schist or shale, containing carbon and sulfur, before treating with water. In another English patent[2] carbon is added to the aluminous material to aid in the calcination. A Norwegian patent[3] recommends that carbonaceous aluminous shales be heated in a gas producer to burn out the carbon before leaching with acids. Meyer[4] claims that superheated steam decomposes aluminum silicate or clay and forms alumina soluble in acid. A small amount of hydrochloric acid is said to speed up the reaction.

An iron ore, such as Cuban iron ore, can be subjected to a sulfating roast, whereby a large portion of the metals present other than iron are rendered soluble.[5] The soluble sulfates are decomposed by heating or converted to the oxides by precipitation methods and the alumina recovered by the Bayer process.

Extraction and Flotation of Impurities.

A number of inventors have worked on the problem of improving the quality of aluminous ores by mechanical separation processes. Langford[6] gives clay or bauxite a preliminary wash with dilute sulfurous or sulfuric acid. Redwood pulp is added either at this or a later stage of the process to remove certain other impurities. Schwerin[7] separates the clay from sand, iron pyrites, and other impurities by adding an agent such as ammonia or sodium silicate which will suspend the clay in water, but not the impurities. Certain substances may be added to an impure suspension of clay which will neutralize the electrical charges upon the impurities and cause them to precipitate. It is also stated that fractional sedimentation will improve the quality of the clay. Ivery[8] suspends clay in water by means of oil, soap, grease, etc., and floats it away from the grit and foreign matter. According to

[1] Rich, S. W., Br. Pat. 547 (1872), Aug. 13, 1872.

[2] Llewellyn, I. P. and Peter Spence and Sons, Br. Pat. 12,308 (1912), May 26, 1913.

[3] Norsk Hydro-Elektrisk Kvael., Norw. Pat. 40,355, Nov. 24, 1924.

[4] Meyer, E., Br. Pat. 14,084 (1890) Sept. 5, 1891. See also De St. Laurent, E. E. and R. D. Mackintosh, Br. Pat. 11,820 (1915) Mar. 8, 1917.

[5] Hayward, C. R., F. O. Stillman, H. M. Schleicher, U. S. Pats. 1,341,901, June 1, 1920; 1,370,646, Mar. 8, 1921; Br. Pat. 155,246, Mar. 30, 1922. Hayward, C. R., *Chem. Met. Eng.* **26**, 261–266 (1922).

[6] Langford, F., U. S. Pats. 1,249,125, Dec. 4, 1917; 1,308,429, July 1, 1919.

[7] Schwerin, O., U. S. Pats. 993,888, May 30, 1911; 1,233,713, July 17, 1917; Reissue 14,583, Jan. 7, 1919; Br. Pat. 2,379 (1911), Jan. 11, 1912. See also Piraud, Y. M., Fr. Pat. 633,745, Feb. 2, 1928.

[8] Ivery, J. W., U. S. Pat. 667,222, Feb. 5, 1901.

Everhart,[1] it is possible to separate bauxite and clay by means of a dilute solution (0.2 per cent) of caustic alkali. The bauxite is ground to grains of a size which quickly settle in the solution. The clay is peptized by the alkali and remains in suspension, and can be washed away from the bauxite. Lecesne[2] roasts bauxite and then subjects it to a pulverizing action produced by shock. The alumina is not as easily pulverized as the impurities and can be separated by screening, air elutriation, or levigation. It is said that a crushing operation does not produce satisfactory results.

PRELIMINARY TREATMENT OF ORE TO REMOVE IRON

In the acid processes for the production of alumina, the presence of iron becomes as much of a problem as the presence of silica was in the alkali aluminate process. Many patents have been issued on processes for the removal of iron and other impurities before dissolving the alumina. How successful these processes would be is a matter of conjecture; certainly many of them are of little or no value.

Volatilizing Iron as Ferric Chloride or Fluoride.

Le Chatelier[3] removes the gangue from the ore either by a preliminary treatment with hydrochloric acid or by a calcination at a red heat and subsequent treatment with water. The iron is then reduced by heating with carbon, after which it is converted into the volatile chloride by heating in a current of hydrochloric acid gas. It is also claimed[4] that iron may be removed from an aluminous compound by heating it to 700°C. in a stream of chlorine gas. The anhydrous ferric chloride is volatile and the alumina which remains behind is practically iron free. If the iron is present in large amounts, it is best to reduce the oxide with hydrogen at 500 to 600°C. before treating with the chlorine. Ichikawa,[5] in treating Japanese clay, recommends the addition of charcoal to clay to increase the amount of iron volatilized with the chlorine.

Schwahn,[6] after calcining and grinding the clay, treats it with a mixture of sodium chloride, sodium nitrate, and sulfuric acid. Heating is said to expel the ferric chloride along with the nitric and hydrochloric acids. In a later patent[7] he allows the clay to stand in contact with hydrochloric acid at 80°C. for some time and then heats the mixture at

[1] EVERHART, E., U. S. Pat. 1,397,414, Nov. 15, 1921.

[2] LECESNE, N., Fr. Pat. 424,514, May 16, 1911.

[3] LE CHATELIER, Br. Pat. 1,988 (1858), filed Mar. 1, 1859.

[4] KONIGSBERGER ZELLSTOFF-FABRIKEN UND CHEMISCHE WERKE KOHOLYT A.-G., Swiss Pat. 119,467, Mar. 16, 1927.

[5] ICHIKAWA, Y., *J. Chem. Ind.* (Japan) **25**, 1310 (1920).

[6] SCHWAHN, H. F. D., U. S. Pat. 514,039, Feb. 6, 1894.

[7] SCHWAHN, H. F. D., U. S. Pat. 752,927, Feb. 23, 1904.

120 to 150°C. to volatilize the ferric chloride.   Simon[1] adds hydrofluoric acid to bauxite and then heats at 1200 to 1400°C. to drive out the volatile iron and silicon fluorides.   As an alternative method, he states that the bauxite may be treated with aqueous hydrochloric acid, dried and mixed with 10 to 20 per cent sodium chloride and heated to drive out volatile iron chloride.   Simon and Pernot[2] heat bauxite at a temperature of 400°C. in an atmosphere of hydrogen chloride and a hydrocarbon.   The iron and silicon chlorides formed by this treatment are volatile and are easily removed from the alumina.

MacDowell and Hershman[3] make the improbable claim that by heating aluminous material, such as alunite, containing silica and iron as impurities, in the presence of carbon and an inert gas to a temperature above 1650°C., all the silica is volatilized as silicon.   The addition of a chloride and sulphuric acid insures the elimination of the iron as volatile chloride.

Rinman[4] heats clay or other aluminous material with hydrogen chloride and a reducing gas to a red heat in order to eliminate iron as the volatile chloride.   According to Saunders and Petrikin,[5] the impurities in bauxite or clay, such as iron, silicon, and titanium, can be removed as the volatile chlorides by heating the material in a current of gaseous aluminum chloride at a temperature of 800°C. or less.

Some of these patentees seem to have overlooked the fact that only anhydrous ferric chloride can be volatilized, the hydrated salt being decomposed by hydrolysis.

Extraction of Iron with Acid Solutions.

A number of inventors have worked on the idea of extracting iron and other impurities from bauxite, clay, etc., by leaching with acid reagents under conditions which would not dissolve much of the alumina. For treating the crude pulverized bauxite, hydrochloric acid of 1.1 specific gravity,[6] as well as various other concentrations,[7] and hot water containing less than 1 per cent of sulfuric acid,[8] have been recommended.

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[1] Simon, A., Fr. Pat. 394,805, Feb. 3, 1909.

[2] Simon, A. and L. Pernot, Fr. Pat. 406,590, Feb. 2, 1910; 1st Add. 11,423, Feb. 11, 1910.

[3] MacDowell, C. H. and P. R. Hershman, U. S. Pat. 1,291,979, Jan. 21, 1919.

[4] Rinman, E. L., Swed. Pat. 29,696, Oct. 29, 1910.

[5] Saunders, L. E. and J. G. Petrikin, U. S. Pat. 364,911, Oct. 27, 1908.

[6] Pedemonte, A., U. S. Pat. 1,490,024, Apr. 8, 1924; Fr. Pat. 547,862, Dec. 27, 1922; Swiss Pat. 101,612, Oct. 1, 1923.

[7] Tardieu, A., Br. Pat. 2,379 (1868), Jan. 29, 1869.

Fulloni, R., Ital. Pat. 140,547, Mar. 20, 1914 (*C. A.* **9**, 2804 (1915).

[8] Langford, F., U. S. Pat. 1,251,058, Dec. 25, 1917.

A mixture of hydrochloric and hydrofluoric acids[1] is said to remove the iron and silicon from bauxite, the iron and silicon compounds being either more soluble or volatile than the aluminum compounds.

Sulfurous acid and sulfites in the presence of mineral acids are also used to extract iron from kaolin.[2] Hyposulfurous acid prepared by the interaction of sulfurous acid and zinc[3] or aluminum,[4] or by electrolysis[5] of sulfurous acid is supposed to be especially effective in dissolving iron, the reaction preferably taking place in an acid solution.[6]

To increase the solubility of the iron, it first may be converted to sulfide by treating with hydrogen sulfide or alkali or alkaline earth sulfides,[7] after which dilute mineral acids, especially sulfurous acid[8] are recommended for dissolving the iron. It is stated[9] that the iron content (calculated as Fe_2O_3) of clay may be thus reduced from 5.14 to 0.26 per cent. Instead of leaching it with dilute acid, the iron sulfide first may be converted into sulfate by treatment with gaseous sulfur dioxide[10] and then leached out with water.

Instead of converting the iron oxide into sulfide, it may be made magnetic by heating in a reducing atmosphere, and it is claimed that after such treatment the iron and titanium may be separated magnetically.[11] Certainly this would not be true of most bauxites because the iron oxide and aluminum oxide are far too intimately associated. The reduced iron may be extracted with hydrochloric or other suitable

[1] LAUR, Fr. Pat. 220,790, Apr. 8, 1892 (also 1st and 2nd Add.).

[2] SCHULZ, F. A.-G. and H. GRUBER, Ger. Pat. 245,164, Mar. 26, 1912 (C. A. **6**, 2,304); Br. Pat. 16,129 (1911), Jan. 11, 1912.

[3] GAUDIN, R. F. B. and DARTMOOR CHINA CLAY CO., Br. Pat. 218,747, July 14, 1924. STUBBS, A. J., Br. Pat. 181,132, June 12, 1922.

[4] REBUFFAT, O., *Atti Primo Cong. Naz. Chim., Pura e.l App.* 282–283 (1923); *C. A.* **11**, 391, (1917); *Atti incorraggiamento Napoli* **67**, 293–294 (1915).

[5] WORSLEY, Br. Pat. 218,347 July 3, 1924.

[6] *Bur. Mines Bull.* **267**, p. 17.

[7] CONDY, H. B. and G. ROSENTHAL, Br. Pat. 4,618, June 6, 1878; Fr. Pat. 5,589, June 25, 1878.

[8] PENIAKOFF, D. A., U. S. Pat. 695,762, Mar. 18, 1902.

[9] PARENTANI, F., Br. Pat. 255,300, July 22, 1926.

[10] FLEISSNER, H., Ger. Pat. 439,033, Jan. 3, 1927; Aust. Pat. 102,553, Feb. 25, 1926.

[11] LECESNE, N., Fr. Pat. 424,514, May 16, 1911.

PEDEMONTE, A., Br. Pat. 195,295, Mar. 29, 1923; Fr. Add. Pat. 26,369, Nov. 13, 1923.

PENIAKOFF, D. A., Aus. Pat. 4,616, July 10, 1901.

PLATSCH, M., Fr. Pat. 543,481, Sept. 4, 1922; Ger. Pat. 381,348, Sept. 9, 1923.

acid.[1] In general, such heating would make the aluminum oxide quite insoluble.

Several foreign patents[2] claim that by heating bauxite in an atmosphere of carbon monoxide at a high temperature and pressure, the iron impurities are eliminated as volatile iron carbonyl.

Extraction of Iron with Organic Compounds.

Langford[3] treats clay with a solution of tannin to remove common impurities, such as iron, which are soluble or can be separated by flotation. One of the oldest methods suggested for the removal of iron is that of Chadwick and Kynaston[4] in which finely ground bauxite or clay is mixed with oxalic and hydrochloric acids and allowed to stand for a week. Water is then added and the iron washed out from the alumina; this treatment is said to remove about two-thirds of the iron. Aldehyde sulfoxylic and ketone sulfoxylic acids or derivatives of these acids in the presence of mineral acids are said to extract iron from kaolin, clay, etc.[5]

SULFURIC ACID PROCESSES

General Details of Process.

Sulfuric acid has been given more extensive consideration than other acids for the extraction of alumina, because of its lower cost and the greater ease with which it can be handled in commercial equipment. The first considerations in the choice of conditions for the extraction of the alumina are the concentration and temperatures of the acid to be employed. The use of sulfuric acid, from dilute solutions containing 15 per cent of acid up to concentrated sulfuric acid, has been tried and recommended. The use of concentrated sulfuric acid is disadvantageous because of the formation of insoluble hydrated acid aluminum sulfate. This can be avoided by having sufficient water present during the reaction. Temperatures of digestion

[1] LE VERRIER and MINET, Fr. Pat. 244,582, Jan. 24, 1895.

ANTOINE, L., Fr. Pat. 240,296, July 25, 1894.

HULTMAN, G. H., Swed. Pat. 41,834, Jan. 10, 1917.

PEDEMONTE, A., U. S. Pat. 1,490,024, Apr. 8, 1924; Fr. Pat. 547,862, Dec. 27, 1922; Add. Pat. 26,179, Sept. 5, 1923; Swiss Pat. 101,612, Oct. 1, 1923.

[2] BADISCHE ANILIN AND SODA FABRIK, Br. Pat. 256,128, Aug. 12, 1926. I. G. FARBENINDUSTRIE A.-G., Swiss Pat. 120,854, June 1, 1927.

[3] LANGFORD, F., U. S. Pat. 1,251,057, Dec. 25, 1917.

[4] CHADWICK, W., J. CHADWICK, T. CHADWICK, J. KYNASTON, U. S. Pat. 228,867, June 15, 1880; Ger. Pat. 11,137, Nov. 27, 1880.

[5] SCHULZ, F., A.-G., H. GRUBER, Br. Pat. 2,309 (1924), July 29, 1915.

,s high as 450°C. have been employed. The particular acid
concentration to be used in any case must be determined by
ests on the raw material available.

The heat of reaction between sulfuric acid and alumina, and
he heat of dilution of concentrated sulfuric acid may be sufficient
,o heat the solution to the required digestion temperature
without the external application of heat.[1]

Herbos,[2] for example, divides the bauxite into two portions,
adding water to one and concentrated sulfuric acid to the other.
The two parts are then mixed together in such a manner that the
heat of reaction is sufficient to cause the solution of the bauxite
without the addition of external heat. When bauxite is mixed
with water and added to concentrated sulfuric acid,[3] similar
results are obtained. In recent foreign patents,[4] the sulfuric
acid is allowed to percolate through the raw material (clay or
argillaceous materials) which is kept in a stationary state. The
flow is so adjusted that a temperature of at least 105°C. is
maintained in the zone of maximum reaction. It is claimed
that large batches of material may be handled by this method,
and that a volatile acid, such as hydrochloric acid, may be used.

Effect of Concentration of Acid.

The following processes are cited to show the variety of
concentrations of sulfuric acid which have been used under one
condition or another. Carter, Shackelton, and Grafton[5] use
30°Bé. sulfuric acid to decompose halloysite. Lewis[6] grinds the
aluminous material with 45 to 50°Bé. sulfuric acid and then
heats the mixture at 180 to 260°F. for several days; the higher
temperatures produce neutral or basic alum. Basset[7] treats
calcined clay with 50 to 52° Bé. sulfuric acid at 100 to 150°C.,

[1] CROLL, A. A., U. S. Pat. 221,787, Nov. 18, 1879.

EASTWICK, J. H., U. S. Pat. 239,089, Mar. 22, 1881.

PEMBERTON, H., U. S. Pat. 78,005, May 19, 1868; 82,747, Oct. 6, 1868.

[2] HERBOS, J. G., Fr. Pat. 638,760, June 2, 1928.

[3] TRAWINSKI, F., Fr. Pat. 633,199, Jan. 23, 1928.

[4] I. G. FARBENINDUSTRIE, A.-G., Br. Pat. 278,370, Jan. 12, 1928; Fr. Pat.
641,623, Aug. 7, 1928. Aust. Pat. 110,889, Oct. 10, 1928.

[5] CARTER, P. H., H. H. SHACKELTON, T. E. GRAFTON, U. S. Pat. 1,037,591,
Sept. 3, 1912.

[6] LEWIS, G. T., U. S. Pat. 209,488, Oct. 29, 1878.

[7] BASSET, A. M., Fr. Pat. 230,321, May 25, 1893; Add. Pat. June 23
1894.

and after leaching adds potassium sulfate solution and recovers crystalline alum. Haslup and Peacock[1] digest a mixture of greensand, or similar material and bauxite with 50 to 55°Bé. acid in heat-insulated receptacles. It is said that no external heat is required. Muth[2] treats kaolin or bauxite with 62 to 63°Bé. sulfuric acid in the form of a spray and then heats to 150 to 200°C. to produce a crude aluminum sulfate. Funcke[3] treats clay which has been calcined and finely powdered with 66°Bé. sulfuric acid. Moderate heat is applied by means of steam until the acid is neutralized by the alumina. Moxham[4] boils aluminous materials with sulfuric acid of 1.35 to 1.45 specific gravity. Sulfuric acid of 1.4 specific gravity is specified by Pedemonte[5] for dissolving bauxite. Another French patent[6] states that iron-free aluminum sulfate can be made by digesting clay at 70 to 100°C. with sulfuric acid of 1.5 specific gravity if enough saltpeter is added to oxidize the iron to the ferric state. The iron in solution is removed by lime and sodium manganate. Milbauer and Skutil[7] recommend the use of sulfuric acid of 1.53 specific gravity.

Addition of Fluorides and Chlorides.

A patent to Gibbs[8] states that hydrofluosilicic acid acts as a catalyst for the reaction between sulfuric acid and feldspar or other refractory silicates. For producing alumina compounds suitable for sizing paper,[9] uncalcined clay is treated with sulfuric acid or bisulfates in the presence of small amounts of hydrofluoric acid or a fluoride. The Amber Size and Chemical Company[10] state that the reaction between unburned clay and sulfuric acid goes on at the temperature developed (130°C. or

[1] Haslup, E. W., and B. A. Peacock, U. S. Pat. 1,279,109, Sept. 17, 1918.

[2] Muth, G., Ger. Pat. 312,960, June 19, 1919.

[3] Funcke, M. J., U. S. Pat. 1,945, Jan. 23, 1841.

[4] Moxham, A. J., Fr. Pat. 558,159, Aug. 23, 1923.

[5] Pedemonte, A., U. S. Pat. 1,490,021, Apr. 8, 1924.

[6] Soc. Fabryka Chemiczna Rudniki Klobukowski i Reicher, Fr. Pat. 236,309.

[7] Milbauer, J., F. Skutil, *Chem. Ztg.*, **42**, 525 527 (1918).

[8] Gibbs, W. T., U. S. Pat. 772,612, Oct. 18, 1904.

[9] Aktiebolaget Gräen, Swed. Pat. 52,770, Sept. 27, 1922.

Muth, G. and L. Duvinage, Fr. Pat. 515,314, Mar. 31, 1921; Br. Pat. 149,001, Oct. 12, 1921.

[10] Amber Size and Chemical Co., Ltd., Br. Pat. 218,629, May 28, 1925.

more) provided a small amount of fluoride is added. A later patent to Muth[1] states that it is necessary to neutralize the product obtained by the reaction between uncalcined china clay and sulfuric acid in the presence of a fluoride when the reaction is carried out in open digesters. A neutral product is obtained by a pressure digest, however, and the process becomes more efficient. Bishop[2] claims that white clay is more easily decomposed with sulfuric acid if fluorspar is added to furnish a small amount of hydrofluoric acid. Further corroboration of this statement is given in U. S. Bureau of Mines Bulletin 267, page 28. Brown[3] treats an aluminum silicate ore which has been heated in the dry state in a rotary kiln with a mixture of gaseous sulfur trioxide and hydrofluoric acid. The hydrofluoric acid is supposed to act as a catalyst in the formation of the metallic sulfates. Dougherty[4] adds 2 to 5 per cent hydrochloric acid or an equivalent amount of sodium chloride to leucite before heating with sulfuric acid.

Removal of Silica from Solution.

It is stated[5] that the addition of organic substances such as sugar, molasses, etc., capable of being carbonized by sulfuric acid at 100°C., facilitates the removal of silica when aluminous materials are dissolved in sulfuric acid. Although silica usually can be eliminated in the acid process, its separation often becomes very troublesome because of the colloidal jells which it forms. In the treatment of leucite, Blanc[6] does not grind the material very fine, removes all dust, and lets the acid circulate through the granular mass without agitating the particles. In this manner the film of silica on the particles is not broken up. The alumina and potash dissolve, but the silica and part of the iron remain in the residue. Using hydrochloric acid, this method of dissolving leucite has been successfully operated on a semi-commercial scale.

[1] Muth, G., U. S. Pat. 1,661,618, Mar. 6, 1928.

[2] Bishop, H. B., U. S. Pat. 1,480,928, Jan. 15, 1924.

[3] Brown, C. M., U. S. Pat. 1,492,016, Apr. 29, 1924.

[4] Dougherty, E. E., U. S. Pat. 1,148,156, July 27, 1915.

[5] Brünjes, F., Ger. Pat. 87,908, July 7, 1896.

[6] Blanc, G. A., U. S. Pat. 1,443,674, Jan. 30, 1923; Br. Pat. 181,677, Mar. 22, 1923; Fr. Pats. 552,653, May 4, 1923; 578,472, Sept. 26, 1924; Ger. Pat. 357,833, Aug. 31, 1922; Norw. Pat. 38,056, Oct. 15, 1923.

Use of Pressure.

Pressure is sometimes used in the sulfuric acid digestion process. For example, in 1877 a patent was granted to Lennig[1] for treating clay or kaolin with sulfuric acid under pressure. Spence[2] digests aluminous material with hot sulfuric acid under pressure to produce a basic aluminum sulfate solution. The basicity is further increased with calcium carbonate and filtered before the basic sulfate is crystallized. Meiklejohn[3] produces a slightly basic aluminum sulfate by digesting aluminous material with sulfuric acid under pressure at a temperature above 160°C. The preferred concentration of the sulfuric acid is expressed as an acid-to-water ratio which is greater than 1:1.3. Moldenke[4] heats a paste of bauxite and 60 to 66°Bé. sulfuric acid in a closed vessel to 500 to 600°F. The granular material thus obtained is leached and the solution filtered and crystallized. Hayward and Schleicher[5] treat the hot slate which has been calcined at 250°C. with concentrated sulfuric acid under pressure. After digesting for 3 hours at a temperature of 160°C., the solution is filtered and the aluminum crystallized from solution as potash alum. Jacobsson[6] states that the oxides of calcium, silicon, and titanium do not dissolve when calcined clay or bauxite is digested with sulfuric acid under pressure. Later patents to Jacobsson[7] describe a continuous process for the solution of aluminous material in sulfuric acid under pressure at 150 to 185°C.

According to Rankin,[8] difficultly soluble substances such as ignited alumina are made soluble by moistening with sulfuric acid and heating to a high temperature under pressure. Salts

[1] LENNIG, C., U. S. Pat. 191,160, May 22, 1877.

[2] SPENCE, H., U. S. Pat. 754,824, Mar. 15, 1904; Fr. Pat. 331,836, Oct. 3, 1903; Ger. Pat. 167,419, Jan. 25, 1906.

[3] MEIKLEJOHN, R. M., Can. Pat. 263,596, Oct. 22, 1926.

[4] MOLDENKE, R., U. S. Pat. 1,388,436, Aug. 23, 1921.

[5] HAYWARD, C. R., and H. M. SCHLEICHER, U. S. Pat. 1,415,346, May 9, 1922.

[6] JACOBSSON, R., U. S. Pat. 1,570,353, Jan. 19, 1926; Br. Pats. 221,209, Aug. 6, 1925; 243,183, Nov. 26, 1925; Fr. Pat. 584,901, Feb. 18, 1925; Swiss Pat. 117,772, Dec. 1, 1926; Aust. Pat. 105,338, Jan. 25, 1927; Norw. Pat. 44,025, May 25, 1927.

[7] JACOBSSON, R., Br. Pat. 269,174, Sept. 1, 1927; Fr. Pat. 632,205, Jan. 5, 1928; Norw. Pat. 45,995, Jan. 21, 1929; Swiss Pat. 128,989, Dec. 1, 1928.

[8] RANKIN, H. D., U. S. Pats. 1,364,804, Jan. 4, 1921; 1,378,485, May 17, 1921.

which decompose at a high temperature and pressure may be substituted for the sulfuric acid.

Miscellaneous Methods of Treatment with Sulfuric Acid.

The treatment of various substances, such as potash feldspars,[1] iron-free talc,[2] greensand,[3] mixtures of mica and potash salts,[4] or clay and alkali sulfate[5] with sulfuric acid to produce aluminum sulfate or alum has been described by numerous inventors. Counter current systems of digestion[6] have been recommended, while a continuous process is described by Spicer[7] for making aluminum sulfate from bauxite and sulfuric acid by means of Dorr agitators and thickeners. The practical details of the equipment and the operation of such a process have been described by Walker.[8] According to Wrigley,[9] a shale or clay is crushed to pass a 6 to 8-mesh screen and boiled with dilute sulfuric acid in a vessel which has a false bottom, so that the coarser material is prevented from settling to the bottom of the pan. The insoluble fines are allowed to settle from the solution before crystallization is allowed to take place.

Devaucelle[10] grinds the solid cake produced from the reaction between sulfuric acid and clay and then calcines at 300°C. The resulting material is leached with water and filtered.

Digestion with Sulfates or Acid Sulfates.

Aluminum sulphate may be prepared from aluminous materials by heating or digesting with acid ammonium or alkali sulfates.

[1] RAVNER, O., Swed. Pat. 45,388, May 14, 1919; Norw. Pat. 29,359, Jan. 20, 1919.

[2] Jooss, M. F., Fr. Pat. 338,387, May 17, 1904.

[3] WURTZ, J. H., U. S. Pat. 7,337, Oct. 22, 1850.

[4] ARSANDAUX, H. M., Fr. Pat. 428,227, Aug. 25, 1911.

[5] HEIBLING, J., Fr. Pat. 508,023, Sept. 29, 1920.

NIBELIUS, A. W., U. S. Pat. 544,319, Aug. 13, 1895.

[6] SPENCE, H., W. B. LLEWELLYN, U. S. Pat. 1,070,300, Aug. 12, 1913; Br. Pat. 112,881, Jan. 31, 1918; 119,924, Oct. 24, 1918; BRADNER, D.B., U. S. Pat. 1,663,435, Mar. 20, 1928; Br. Pats. 3,805 (1912), Feb. 13, 1913; 22,590 (1912), Oct. 6, 1913.

[7] SPICER, H. N., U. S. Pat. 1,604,427, Oct. 26, 1926; Ger. Pat. 407,484, Dec. 23, 1924; Fr. Pat. 623,774, June 30, 1927; Br. Pat. 257,643, Aug. 30, 1926.

[8] WALKER, G. E., *Chem. Met. Eng.*, **31**, 776–80 (1924).

[9] WRIGLEY, H., Br. Pat. 230,916, Mar. 19, 1925.

[10] DEVAUCELLE, L. P., Fr. Pat. 587,631, Apr. 21, 1925.

Hultman[1] starts with clay and acid potassium or ammonium sulfate solution and obtains a crystalline alum. The process becomes cyclic, since the product is dissolved in water and heated under pressure to form insoluble basic aluminum sulfate and a solution of acid sulfate which can be used upon raw material. White[2] neutralizes a 35°Bé. solution of niter cake with clay, bauxite, or alunite. Tanaka[3] heats a 30°Bé. solution of sodium acid sulfate with aluminum or alumina to neutralize the acid and, after filtering and cooling, obtains about two-thirds of the sodium sulfate as crystals. The aluminum salt crystallizes as potassium alum after adding the required amount of potassium chloride. Several foreign patents[4] state that aluminum sulfate can be made by treating aluminum compounds with an acid sulfate either by the wet or dry process. Everhart[5] treats a hot niter cake solution with bauxite and after dilution neutralizes any free acid with lime. Glauber's salt is removed by crystallization. Hipp[6] has a patent covering the purification of the niter-cake solution by means of alkali sulfide before it is used for the digestion of aluminous material. Bergman[7] electrolyzes a sodium sulfate solution in a diaphragm cell and uses the acid liquid which collects at the anode to dissolve aluminous compounds. The alkaline cathode liquid is used to precipitate the alumina from the acid solution.

An interesting process, which employs ammonium bisulfate in the extraction of clay, is that of Buchner; it is described in some detail in the next section.

"Aloton" Process of Buchner.

As has been previously stated, the two important practical difficulties in connection with sulfuric acid processes for extracting alumina from clay or similar materials are (1) the adequate and

[1] HULTMAN, G. H., Swed. Pat. 54,114, Mar. 28, 1923.

[2] WHITE, J. F., U. S. Pat. 714,846, Dec. 2, 1902. See also POCHIN, W., J. H. RICHARDSON, Br. Pat. 25,228 (1907), applied for Nov. 14, 1907.

[3] TANAKA, G., Jap. Pat. 37,834, Jan. 14, 1921.

[4] DE TORRÓNTEGUI É. IBARRA, L. J., B. HELGUERA Y. ORTIZ, M. M. MANTILLA, Br. Pat. 102,944 (Void); Fr. Pat. 483,631, July 26, 1917; Swiss Pat. 77,660, May 1, 1918.

[5] EVERHART, E., U. S. Pat. 690,257, Dec. 31, 1901.

[6] HIPP, G. E., U. S. Pat. 781,341, Jan. 31, 1905.

[7] BERGMAN, W. D., Norw. Pat. 30,846, June 28, 1920; Swed. Pats. 44,183, June 26, 1918; 44,788, Dec. 11, 1918.

cheap purification of the aluminum sulfate solution from iron, and (2) the complete and cheap recovery of the sulfuric acid employed so that it may be used cyclically. One of the neatest solutions of these two problems is presented in the Aloton process of M. Buchner,[1] which has been developed in Germany on a semi-commercial scale. This process rests upon three fundamental ideas, two of which are quite novel. The acid is circulated in the form of ammonium sulfate.

The first operation consists in heating the solid ammonium sulfate in a suitable vessel (made of aluminum, magnesium, or high silicon iron) so that ammonia is driven off and most of the sulfate converted to bisulfate. The ammonia is, of course, recovered and used elsewhere in the process. Clay is treated with this fused bisulfate and a little water in a digester at temperatures around 200°C., and the resulting slurry of ammonium aluminum sulfate, ammonium iron sulfates, and insoluble material is added to an excess of a hot saturated solution of ammonium sulfate, and filtered. On cooling, presumably with stirring, the ammonium alum precipitates out in a state of very high purity, while the iron salts remain in solution in the excess of ammonium sulfate. The ammonia alum may be recrystallized from ammonium sulfate solution if desired, and is then decomposed by treating the small crystals with two or three times the theoretical quantity of ammonia in the form of a concentrated solution. The aluminum hydrate is thus precipitated in a granular form which can be easily filtered and washed clean of ammonium sulfate. The ammonia and ammonium sulfate are used cyclically. When too much iron accumulates in any lot of ammonium sulfate solution it is concentrated as far as possible for the recovery of a moderately pure ammonium sulfate which goes back into the process, and then the iron and alumina remaining in solution are precipitated with ammonia. It is claimed that these precipitated hydroxides are also easily washed. The purified ammonium sulfate solution thus obtained goes back into the process. Further details regarding the precipitation of the aluminum hydrate are given on page 212.

[1] BUCHNER, M., U. S. Pat. 1,493,320, May 6, 1924; Br. Pat. 195,998, Apr. 12, 1923; Fr. Pat. 542,176, Aug. 7, 1922; Ger. Pat. 425,222, Feb. 13, 1926; Swed. Pat. 53,945, May 9, 1923; Norw. Pat. 40,118, Nov. 3, 1924; Aust. Pat. 106,692, June 25, 1927. See also WASILEWSKI, L., *Przemysł Chem.* **12**, 40–48 (1928).
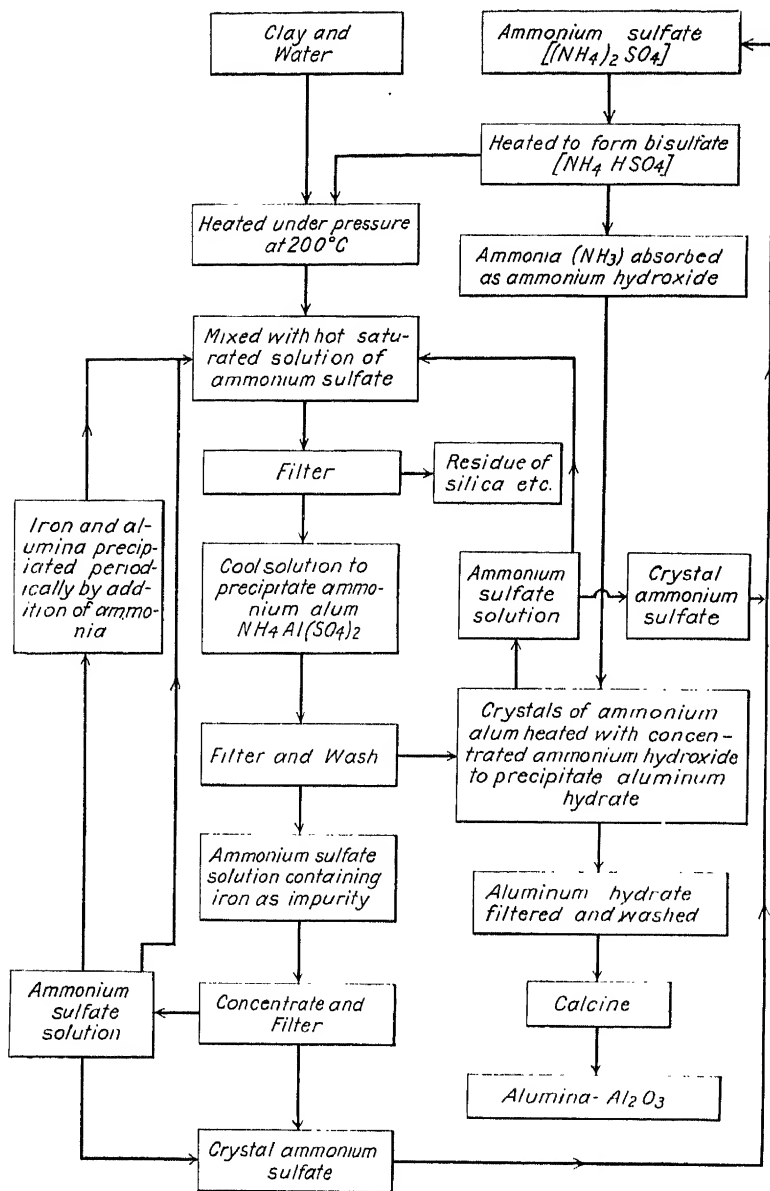
FIG. 41. Diagram of Buchner "Aloton" process for producing alumina.

The principal drawbacks of the process lie in the number of operations required and the unavoidable losses of ammonia. While it is theoretically possible to recover all of the ammonia and ammonium sulfate in such a process, in practice there is always some unavoidable loss of ammonia gas; and in washing precipitates the point is soon reached where the cost of evaporating the wash water and recovering the sulfate becomes greater than the value of the salt recovered. The relatively large amount of fuel required for the various heating and evaporating processes is also a serious matter.

Treatment with Sulfur Dioxide and Sulfurous Acid.

Sulfur dioxide and sulfurous acid have been utilized for the production of aluminum sulfite and sulfate. The conversion of sulfurous acid to sulfuric acid appears to be catalyzed by clay.

Wing[1] passes dilute sulfurous gases through a hot copper sulfate solution and forms sulfuric acid, which is neutralized with bauxite or aluminum hydrate. After removing the copper, the aluminum sulfate solution is concentrated and the salt crystallized. Keogh[2] treats aluminous materials with sulfur gases and obtains aluminum sulfate. According to Beringer,[3] an aluminum sulfite solution is changed into the sulfate by the action of air at 130°C. and a pressure of 5 atmospheres. He describes a continuous process for the production of aluminum sulfate from clay, sulfur dioxide, and air. Morel[4] states that soluble aluminum sulfate is formed by heating bauxite in the presence of sulfur dioxide, air, and steam. Brown[5] treats feldspar with sulfur dioxide and oxygen at a temperature of 1000°F. to form potassium and aluminum sulfates. According to Neil,[6] soluble sulfates are obtained by fusing feldspar or leucite with alkali sulfate or bisulfate and then treating the fused mass with sulfur dioxide and oxygen or sulfur trioxide.

[1] Wing, H. H., U. S. Pat. 712,226, Oct. 28, 1902.

[2] Keogh, L. R., U. S. Pat. 794,413, July 11, 1905.
   See also Peniakoff, D., Br. Pat. 21,476 (1912), Mar. 13, 1913.

[3] Beringer, C. A., Ger. Pats. 269,794, Jan. 30, 1914; 286,366, Aug. 4, 1915.

[4] Morel, J., Br. Pat. 149,769, Aug. 17, 1920; Fr. Pat. 493,616, Aug. 14, 1919.

[5] Brown, C. M., U. S. Pat. 1,402,831, Jan. 10, 1922.

[6] Neil, J. M., U. S. Pat. 1,034,281, July 30, 1912; Br. Pat. 22,557 (1912) May 22, 1913.

Several patents[1] specify the use of sulfurous acid for decomposing aluminous materials. The ore is usually given a preliminary treatment to increase the solubility of the alumina. Boron trioxide is used as a flux by Levitt.[2] The resulting mass obtained from an orthoclase feldspar fusion is ground and suspended in water and sulfur dioxide passed through it until the borates are decomposed. It is stated that ferrous iron remains in solution when the alumina is precipitated from the sulfite solution by heat. A Swedish patent[3] states that pressure may be advantageously used with the sulfurous acid. Langford[4] treats purified clay with sulfurous acid under pressure while air circulates through the solution. Eustis[5] treats Cuban ore with sulfur dioxide at 460°C. and claims that little iron is dissolved in the leaching process. Frost[6] treats dross screenings with water and sulfur dioxide. The copper will remain as metal in the residue provided a sufficient quantity of metallic aluminum is present. After filtering, the sulfite solution is heated, whereupon alumina precipitates, leaving iron and zinc in solution. The residue insoluble in the sulfurous acid is dissolved in sulfuric acid and the copper recovered by electrolysis.

After removing one-third of the silica from feldspar (see p. 175), Morse[7] treats the potassium aluminum silicate with sulfur

[1] COMPAGNIE GÉNÉRALE L'ALUMINIUM SOCIÉTÉ ANONYME, Norw. Pat. 7,552, Sept. 4, 1899; Dan. Pat. 2,340, July 3, 1899.

RAMSAY, J. H., F. R. LOWE, Br. Pat. 9,705 (1915), Aug. 3, 1916.

RAYNAUD, E., U. S. Pat. 650,763, May 29, 1900; Ger. Pat. 107,502, Nov. 14, 1899; Swed. Pat. 10,268, Oct. 14, 1899.

WILDMAN, H. G., U. S. Pat. 1,326,384, Dec. 30, 1919; Br. Pat. 161,310, Apr. 14, 1921; Fr. Pat. 509,142, Nov. 2, 1920.

YNGSTRÖM, L., A. R. LINDBLAD, S. A. J. BERGSCHÖLD, Swed. Pat. 40,757, June 7, 1916.

KALMUS, H. T., W. L. SAVELL, U. S. Pat. 1,090,479, Mar. 17, 1914; KALMUS, H. T., W. L. SAVELL, K. B. BLAKE, U. S. Pat. 1,148,092, July 27, 1915.

TANAKA, H., Jap. Pat. 40,177, Oct. 3, 1921.

STUBBS, A. J., Br. Pat. 181,132, June 12, 1922.

[2] LEVITT, E., U. S. Pats. 1,399,216; 1,399,217, Dec. 6, 1921; Br. Pat. 177,736, Apr. 6, 1922.

[3] YNGSTRÖM, L., A. R. LINDBLAD, S. A. J. BERGSCHÖLD, Swed. Pat. 40,757, June 7, 1916.

[4] LANGFORD, F., U. S. Pat. 1,308,429, July 1, 1919.

[5] EUSTIS, F. A., U. S. Pat. 1,230,143, June 19, 1917.

[6] FROST, J. G. G., U. S. Pats. 1,648,262, 1,648,263, Nov. 8, 1927.

[7] MORSE, H. N., U. S. Pat. 1,286,718, Dec. 3, 1918.

dioxide at 250°C. After dissolving the potassium salt, the remaining aluminum silicate is suspended in water and decomposed with sulfur dioxide. The aluminum sulfite dissolves, while the silica remains as an insoluble residue. Ramsay and Lowe[1] claim that carbonic acid will decompose the sodium aluminum silicate in red mud (the residue from the digestion of bauxite by the Bayer process) and give soluble sodium carbonate and alumina, which is soluble in sulfurous acid. Tests show, however, that the reactions are incomplete.

Water-soluble Compounds Formed by Furnacing with Sulfates.

Various processes have been suggested which employ sulfates or bisulfates for decomposing aluminous compounds at a high temperature. Emanuel[2] fuses clay or bauxite with 6 mols of sodium bisulfate for each mol of alumina. The silica becomes insoluble but the ferric alum and a double sulfate of aluminum and sodium $(Al_2(SO_4)_3.3Na_2SO_4)$ are soluble. According to Linkmeyer,[3] soda alum is made by fusing clay with hydrated sodium bisulfate, water being added to maintain 1 molecule of water for each molecule of bisulfate. According to the German patent to Papierfabrik Köslin A.-G.,[4] iron-free aluminum sulfate is made by heating a mixture of equivalent amounts of clay and bisulfate with an oxidizing agent such as barium peroxide. The mixture is made into a plastic mass with water and heated gradually to 300 to 400°C., whereupon the iron compounds are oxidized and become insoluble in the extracting liquid. Hess[5] extracts a fusion of aluminum silicate and alkali sulfate or bisulfate, using 10 per cent ammonium sulfate solution in order to stop the formation of basic sulfates which would remain with the silica. Jackson[6] fuses uncalcined clay with niter cake and, after leaching, crystallizes the salt with or without the addition of potassium or ammonium sulfate. Whittington[7] heats bauxite or clay with ammonium sulfate at 525 to 560°C. until ammonia

[1] Ramsay, J. H., F. R. Lowe, Br. Pat. 9,705 (1915), Aug. 3, 1916.

[2] Emanuel, P. A., U. S. Pat. 957,848, May 10, 1910; Br. Pat. 20,048, 1910 (Void); Lage, H., Fr. Pat. 419,169, Dec. 28, 1910.

[3] Linkmeyer, R., Ger. Pats. 301,641, Sept. 10, 1919; 303, 981, Oct. 25, 1919.

[4] Papierfabrik Köslin A.-G., Ger. Pat. 301,614, Sept. 30, 1919.

[5] Hess, L., Ger. Pat. 376,717, June 5, 1923.

[6] Jackson, L. L., U. S. Pat. 1,254,229, Jan. 22, 1918.

[7] Whittington, J. A., U. S. Pat. 1,549,398, Aug. 11, 1925.

ceases to be given off.   The aluminum sulfate is soluble in water, while the iron sulfate has been converted into insoluble oxides. According to Rinman[1] kaolin, feldspar, or bauxite is heated with an ammonium salt, preferably the sulfate, at 250 to 400°C. and the ammonia gas recovered.   The silica is insoluble in water, while the ammonium alum is soluble and may be crystallized from solution.   The alum may be crystallized without filtering, since the crystals do not occlude suspended matter.   If ammonium chloride is used in place of the sulfate, the decomposition is carried out under pressure until the evolution of ammonia ceases, and then pressure is released so that the aluminum chloride may distill.   In a German patent to Riedel[2] it is stated that a temperature of 350 to 400°C. should not be exceeded when an aluminous compound is heated with ammonium sulfate or potassium ammonium sulfate.   By keeping below this temperature, the decomposition and loss of ammonia is avoided.   A temperature of 280 to 370°C. is satisfactory for the decomposition of an aluminum silicate.   According to Hess,[3] the yield is increased by using 5 to 7 mols of ammonium sulfate to each mol of alumina in the clay instead of the 4 mols required by theory.   By allowing the clay to stand in contact with the ammonium sulfate (wet or dry) for a long time before heating, Hess[4] claims that the yield is increased.   Other foreign patents[5] describe a process for the economical recovery of ammonia as the sulfate.   Aluminum hydrate is heated with ammonium sulfate to about 350°C. and the evolved ammonia dissolved in water and converted into the carbonate by means of carbon dioxide.   Gypsum is used to convert the ammonium carbonate into ammonium sulfate and insoluble calcium carbonate.

Alkali sulfate may be used in addition to the ammonium sulfate.   Heibling[6] substitutes potassium sulfate for a part of the

[1] RINMAN, E. L., U. S. Pat. 914,187, Mar. 2, 1909; Can. Pat. 107,249, Sept. 3, 1907; Fr. Pat. 367,756, Nov. 9, 1906; Ger. Pat. 198,707, June 2, 1908; Swed. Pats. 27,185, July 17, 1909; 29,837, Nov. 26, 1910; 36,260, Feb, 25, 1914; Norw. Pat. 16,165, Mar. 18, 1907; Br. Pat. 15,590 (1906), July 4, 1907.   See also BJORKSTEDT, W. G., U. S. Pat. 1,681,921, Aug. 28, 1928.

[2] J. D. RIEDEL, A.-G., Ger. Pats. 386,644, Dec. 13, 1923; 424,701, Jan. 29, 1926.

[3] HESS, L., Ger. Pat. 388,996, Jan. 23, 1924.

[4] HESS, L., Ger. Pat. 360,201, Sept. 30, 1922.

[5] VEREINIGTE ALUMININUM WERKE A.-G. and W. FULDA, Ger. Pats. 354,328, June 7, 1922; 367,134, Jan. 17, 1923.

[6] HEIBLING, J., U. S. Pat. 521,712, June 19, 1894; Fr. Pat. 227,425, Jan. 25, 1893; Add. Pat. July 12, 1894; Ger. Pat. 70,549, July 26, 1893.

ammonium sulfate ordinarily used. For each mol of alumina, 3 mols of ammonium sulfate and 1 mol of potassium sulfate are mixed with the clay and then heated at 275 to 300°C. The ammonia is recovered and the alum removed by crystallization.

A cyclic process is described by Brown[1] in which alunite is heated to drive off sulfur trioxide and the residue heated with ammonium sulfate to form ammonium alum. The alumina is obtained by treating the alum solution with the evolved ammonia gas and the ammonium sulfate is recovered to treat further quantities of the calcined alunite.

According to Hauber,[2] potash alum can be formed by heating glauconite or greensand with ferrous sulfate to around 450°C. Fleissner[3] prepares aluminum sulfate by heating aluminum silicate with gypsum to a dull red heat. In a patent to Blumenberg,[4] soluble potash alum is obtained by heating feldspar, calcium carbonate, and acid sludge at 700 to 800°C.

Miscellaneous Methods for the Production of Aluminum Sulfate.

A French patent[5] states that very pure aluminum sulfate may be produced by the action of sulfuric acid on purified aluminum chloride solution. The liberated hydrochloric acid is used to form more aluminum chloride. According to Moxham,[6] anhydrous aluminum sulfate can be made from potash alum by dehydrating and extracting potassium sulfate with hot concentrated sulfuric acid. Fulda and Ginsberg[7] treat ammonium alum with 50 to 60 per cent sulfuric acid and obtain aluminum sulfate as an insoluble product as the solution cools. The ammonium sulfate is soluble in sulfuric acid of the above concentration at a temperature of 15 to 20°C., while the aluminum sulfate is only slightly soluble. It is also stated that potash alum can be treated in a similar manner. According to a French patent,[8] basic aluminum sulfate, useful in absorbing aniline dyes, is formed by partially neutralizing aluminum sulfate with soda ash.

[1] Brown, C. M., U. S. Pat. 1,675,157, June 26, 1928.

[2] Hauber, M., U. S. Pat. 1,323,764, Dec. 2, 1919.

[3] Fleissner, H., Ger. Pat. 322,844, July 9, 1920.

[4] Blumenberg, H., U. S. Pat. 1,286,513, Dec. 3, 1918.

[5] Società Italiana Potassa, Fr. Pat. 559,703, Sept. 20, 1923.

[6] Moxham, A. J., U. S. Pat. 1,538,837, May 19, 1925.

[7] Fulda and Ginsberg (Vereinigte Aluminium Werke, A.-G.), Ger. Pat. 442,596, Apr. 4, 1927.

[8] Breton, Fichot and Co., Fr. Pat. 599,868, Jan. 22, 1926.

Moldenke and Schumacher[1] treat aluminous material with sulfuric acid vapors at a temperature of 400 to 500°C. Air is added to keep the iron from forming a soluble compound. Under these conditions, aluminum sulfate is said to form rapidly. while very little iron sulfate is produced.

SULFURIC ACID PROCESS DETAILS

Removal of Iron.

One of the chief difficulties encountered in the sulfuric acid processes for the production of alumina is the elimination of iron, since, as a general rule, the properties of iron and aluminum compounds are very similar. Although many of the processes suggested for the elimination of iron have been shown to be worthless, especially for a commercial process, nevertheless, a large number of the suggestions will be outlined in order to give the reader a general idea of the work that has already been done.

Removal of Iron by Precipitation.

Chadwick and Kynaston[2] precipitate the iron as Prussian blue from an aluminum sulfate solution by means of calcium ferrocyanide. The precipitate is allowed to settle for 2 days and then hydrogen sulfide is passed in, to precipitate arsenic sulfide, which carries down the iron precipitate. If there is no arsenic present, a small amount of copper or zinc sulfate may be added to coagulate the precipitate. A Canadian patent[3] mentions the use of copper sulfate or other soluble metallic sulfates for coagulating the Prussian blue precipitate. Fisher[4] removes the last traces of Prussian blue from the solution by adding metallic zinc, zinc oxide, carbonate, silicate, or sulfide. A porous alum is produced by adding various substances, such as sodium bicarbonate, to the hot concentrated solution just before it solidifies.

Many of the patents state that iron may be precipitated as Prussian blue, but in most cases no practical means have been

[1] MOLDENKE, R. and WM. SCHUMACHER, U. S. Pat. 1,567,610, Dec. 29, 1925; SCHUMACHER, W., Ger. Pat. 383,435, Oct. 13, 1923. See also NÜRANEN, W. J., A. HIBBERT, Br. Pat. 163,348, May 26, 1921.

[2] CHADWICK, J. T. and W., J. W. KYNASTON, U. S. Pat. 237,816, Feb. 15, 1881; Ger. Pat. 14,185, June 9, 1881; Can. Pat. 10,888, Jan. 28, 1880.

[3] HARRISON, J., G. L., and T. S., Can. Pat. 13,186, July 28, 1881.

[4] FISHER, R. A., U. S. Pat. 321,094, June 30, 1885.

suggested for the removal of the colloidal precipitate. To precipitate the iron as Prussian blue, it is first necessary to oxidize all ferrous iron to the ferric state. If the excess of the oxidizing agent is not removed, some of the ferrocyanide will be oxidized to ferricyanide, which will remain in the solution. Some prefer to add ferrocyanide to the solution of ferrous iron and, by oxidizing the solution, obtain the insoluble Prussian blue. Others prefer to add ferricyanide to ferrous iron and obtain the corresponding blue precipitate.

Under most conditions, Prussian blue comes down as a colloidal precipitate which is very difficult to remove by filtration. Salts, such as copper and zinc sulfates, aid in the flocculation of the colloidal Prussian blue. Milbauer and Skutil[1] add copper sulfate or infusorial earth to coagulate the colloidal precipitate and obtain a material which is much easier to filter, and at the same time obtain a higher percentage removal of iron.

According to U. S. Bureau of Mines Bulletin 267, the concentration and acidity of the solution play an important role in the precipitation of the iron. The authors find that filterable precipitates of Prussian blue can be obtained if the pH range is from 3.2 to 3.8. At a pH of 2.0, the precipitate requires several weeks to partially settle and then is not clear, even after filtering. With solutions of a specific gravity greater than 20° Bé. aluminum is precipitated along with the Prussian blue. The fact that aluminum sulfate hydrolyzes in the presence of water and forms colloidal alumina also adds to the difficulty of the precipitation. The quantitative precipitation of iron as Prussian blue in a commercial process can only be successful (if at all) under a close technical control, where the principles of colloid chemistry are applied in a practical manner.

Semper and Fahlberg[2] treat a concentrated and nearly neutral solution of aluminum sulfate containing ferric iron with lead dioxide. The insoluble iron plumbate is removed by filtering and the lead dioxide recovered by means of alkali nitrate. Semper[3] prepares a basic aluminum sulfate solution by dissolving alumina in sulfuric acid and then precipitates the iron by means of plumbic oxide, manganese dioxide or sesquioxide, manga-

[1] MILBAUER and SKUTIL, *Chem. Ztg.*, **42**, 525-27, (1918).

[2] SEMPER, C., C. FAHLBERG, U. S. Pat. 257,567, May 9, 1882; Ger. Pat. 19,218, Aug. 12, 1882.

[3] SEMPER, C., U. S. Pat. 345,604, July 13, 1886.

nates, permanganates, or stannic acid. It is preferable to oxidize the ferrous iron to the ferric state by means of a cheaper reagent before adding the more expensive reagents mentioned above. If sodium bicarbonate is added to the aluminum sulfate solution before it solidifies, a porous product is obtained. In another patent to Semper,[1] a manganous salt is added to the aluminum sulfate solution containing ferric iron in order that the iron and manganese both may be precipitated as an insoluble compound by permanganate. Emanuel[2] recommends the use of either lead dioxide or manganese dioxide for removing iron from aluminum sulfate solutions. Patrouilleau[3] suggests the use of oxidizing agents, such as lead dioxide, manganese dioxide, or hydrogen peroxide. To facilitate the flocculation, a carbonate, such as that of lead, or even carbonic acid gas may be used. According to Glaser,[4] ferric iron is precipitated by tin or antimony oxides. The antimony or tin oxides may be recovered by treating the precipitate with dilute sulfuric acid. Hood and Salamon[5] use tin oxide or sodium tungstate to precipitate ferric iron. According to a German patent,[6] the ferric iron may be removed from a concentrated basic aluminum sulfate solution by filtering through layers of lead, tin, or manganese dioxide. Kynaston[7] uses manganese dioxide which has been washed with dilute sulfuric acid to precipitate the ferric iron out of a neutral solution. In a process described in an early patent,[8] finely divided bauxite is mixed with 3 to 5 per cent arsenious acid and heated with sulfuric acid of 1.45 to 1.5 specific gravity. After the reaction is over, enough hot water is added to reduce the specific gravity to 1.2 and chalk or limestone is then added until no more iron is precipitated. · The arsenic remaining is precipitated by means of hydrogen sulfide. Laur[9] prepares a neutral solution of aluminum

[1] SEMPER, C., U. S. Pats. 264,773, 264,774, Sept. 19, 1882.

[2] EMANUEL, P. A., U. S. Pat. 455, 611, July 7, 1891.

[3] PATROUILLEAU, L. G., SOC. AN. ALUMINE et DÉRIVÉS, Fr. Pat. 577,422, Sept. 5, 1924; Add. Pat. 28,821, Apr. 8, 1925.

[4] GLASER, F. C., Ger. Pat. 23,375, July 26, 1883.

[5] HOOD, J. J. and A. G. SALAMON, Br. Pats. 1,881 (1886), Jan. 14, 1887; 2,966 (1887), Dec. 16, 1887.

[6] FIRMA VEREIN FÜR CHEMISCHE UND METALLURGISCHE PRODUKTION, Ger. Pat. 432,558, Aug. 6, 1926.

[7] KYNASTON, J. W., Ger. Pat. 21,526, Apr. 28, 1883.

[8] CHADWICK, W. T., and J., J. W. KYNASTON, U. S. Pat. 230,106, July 20, 1880.

[9] LAUR, F., Ger. Pat. 7,858, June 1, 1878.

ulfate by digesting bauxite with 50°Bé. sulfuric acid and then precipitates the iron as metal by means of zinc. Instead of using another metal, Pedemonte[1] uses metallic aluminum itself to precipitate the iron and other metal impurities which are below aluminum in the electrochemical series. According to the experimental work of Milbauer and Skutil,[2] the processes above outlined either do not satisfactorily remove the iron, or are too expensive for commercial application.

When the alkalinity of an impure aluminum sulfate solution is gradually increased, the titanium is the first to precipitate, then the ferric iron, and finally the aluminum comes down. In other words, it is easier to precipitate the ferric iron and titanium from a slightly acid solution than it is to precipitate the aluminum, but it is doubtful whether the separation can be made complete in practice.

After removing the iron from the bauxite by one of the methods previously described for the preliminary treatment of the ore, Pedemonte[3] dissolves the bauxite in sulfuric acid of 1.4 specific gravity. The solution is diluted with water and boiled, whereupon the silicic and titanic acids are said to precipitate, leaving a solution of pure aluminum sulfate. Orton and Robinson[4] heat a mixture of finely divided slate and niter cake to a cherry red. After the mixture is treated with water, highly diluted and boiled, a large amount of the iron precipitates.

Schwahn[5] treats powdered kaolin or bauxite with a mixture of sulfur dioxide and ozone in the presence of moisture. The mass is boiled with water and subjected to the action of ozonized air, whereupon the iron is supposed to precipitate and the aluminum sulfate passes into solution. In the British patent to Case,[6] crude aluminum sulfate solution is first oxidized to change the iron to the ferric state. On heating with fluorspar, a solution of aluminum fluosulfate is obtained from which the iron is precipitated with alkali carbonate or hydrate. After filtering off the insoluble iron compound, more alkali is added until all the aluminum compound is precipitated.

[1] PEDEMONTE, A., Fr. Pat. 564,883, Jan. 14, 1924.
[2] MILBAUER and SKUTIL, *Chem. Ztg.*, **42**, 525–527 (1918).
[3] PEDEMONTE, A., U. S. Pat. 1,490,021, Apr. 8, 1924.
[4] ORTON, K. G. P., G. W. ROBINSON, Br. Pat. 139,005, Feb. 26, 1920.
[5] SCHWAHN, H. F. D., U. S. Pat. 1,077,309, Nov. 4, 1913.
[6] CASE, W. E., Br. Pat. 17,111 (1883), Oct. 14, 1893.
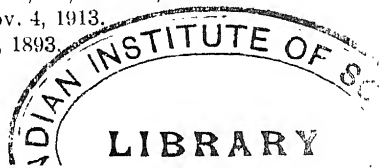
According to a French patent,[1] the iron in the crude aluminum sulfate is oxidized to the ferric state and a solution of potassium sulfate added, the excess acid neutralized, and the iron precipitated by milk of lime or freshly precipitated alumina. It is stated that, after several days of agitation, the solution is substantially iron free. The last traces of iron are removed with sodium or potassium manganate.

According to Augé,[2] the crude aluminum sulfate solution is neutralized with alumina or bauxite after the iron has been oxidized to the ferric state. A solid potassium salt is added to make the iron precipitate settle. It is thought that the potassium salt reacts chemically to form an artificial alunite. Only traces of iron remain in the solution after it is heated and allowed to stand for 25 days. According to White,[3] the iron may be removed from a solution of soda alum by digesting with an excess of alumina until 1 per cent of the total alumina is in the form of basic sulfate, and then adding enough potassium sulfate to precipitate the basic alum along with the iron. The clear solution of soda alum which remains after filtering is fairly free of iron.

In a series of patents, Spence and Llewellyn[4] describe the various conditions of acidity, specific gravity, and temperature of aluminum sulfate solutions best suited for the precipitation of ferric compounds by means of ammonium, potassium, and sodium sulfates.

Barnett and Burgess[5] extract alunogen or halotrichite (aluminum and iron sulfates) with water and, after oxidizing the iron with ozone, add powdered calcium carbonate to precipitate the major portion of the iron. After filtering, the remainder of the iron is precipitated with caustic soda solution. According

[1] Soc. Fabryka Chemiczna Rudniki Klobukowski i Reicher, Fr. Pat. 236,309.

[2] Augé, E., Ger. Pat. 55,173, Jan. 24, 1891.

[3] White, J. F., U. S. Pat. 714,846, Dec. 2, 1902.

[4] Spence, H., W. B. Llewellyn, and Peter Spence and Sons, Ltd., Br. Pats. 9,148 (1914), June 11, 1915; 2,048 (1915), Feb. 3, 1916; 10,166 (1915), July 13, 1916; Br. Pat. 161,606, Apr. 11, 1921. See also Spence, H., U. S. Pat. 754,824, Mar. 15, 1904; Br. Pats. 23,036 (1904), Sept. 14, 1905; 6,458 (1903), Feb. 18, 1904; Fr. Pat. 331,836, Oct. 3, 1903; Ger. Pat. 167,419, Jan. 25, 1906

[5] Barnett, M., L. Burgess, U. S. Pats. 1,252,384 and 1,252,648, Jan. 8, 1918.

) De Souza,[1] the iron is precipitated from an acid solution of
lay by the addition of a limited amount of alkali carbonate.

A British patent[2] states that little iron remains in an aluminum
ılfate solution after it is treated with alumina, calcined bauxite,
r a soluble base and heated to 40°C. The iron should be in the
erric state and what little is left in solution after the above
·eatment can be precipitated with ferrocyanide.

Mejdell[3] heats the nitrate or other acid solution of aluminum
nd iron to 80°C. after it is nearly neutralized. The addition
f a special iron oxide accelerates and otherwise aids in the
recipitation of the iron. The iron oxide loses its catalytic
roperties after it has been once used or has been heated to over
00°C. If the iron oxide ·is placed in an acid solution, whose
cidity is slightly greater than that of the solution in which it is
sed, it regains its catalytic property.[4] The same thing may be
ccomplished by adding the iron oxide to the acid solution and
llowing it to stand for a certain time before the partial neutrali-
ation of the solution takes place. It is claimed that the iron
recipitates obtained in this manner are easy to filter. Patrouil-
:au[5] digests the bauxite with sulfuric acid (50 to 53°Bé.) and
issolves the iron and titanium oxides as well as the alumina.
.fter reducing the iron to the ferrous condition, the solution is
eutralized and the iron oxidized, preferably by ozone. The
olution is heated at 80 to 100°C. during the oxidation and the
·on and titanium are removed as basic salts.

By a close control of the hydrogen ion concentration, Ralston
nd Tilley[6] are able to precipitate the titanium oxide in an
luminum sulfate solution by boiling. The iron is then pre-
ipitated by making the solution more basic. Frischer[7] first

[1] DE SOUZA, A. E., Br. Pat. 2,337 (1905) Dec. 14, 1905; Fr. Pat. 353,277,
,ept. 7, 1905; Norw. Pat. 15,666, Oct. 29, 1906.

[2] DET NORSKE AKTIESELSKAB FOR ELEKTROKEMISK INDUSTRI, Br. Pat.
23,720 (Void); applied for Nov. 26, 1918.

[3] MEJDELL, T., U. S. Pat. 1,421,804, July 4, 1922; Br. Pat. 139,470,
Mar. 10, 1921; Fr. Pat. 510,426, Dec. 4, 1920; Ger. Pat. 355,850, July 8,
922; Swed. Pat. 51,459, Apr. 19, 1922; Norw. Pats. 31,797, Feb. 21, 1921;
2,491, June 20, 1921.

[4] MEJDELL, T., U. S. Pat. 1,444,160, Feb. 6, 1923; Fr. Pat. 544,525,
iept. 23, 1922; Ger. Pat. 399,804, July 30, 1924; Swiss Pat. 99,040, May 1,
923; Norw. Pat. 34,492, Mar. 27, 1922.

[5] PATROUILLEAU, L. G., Fr. Pat. 577,422, Sept. 5, 1924; Add. Pat. 28,821,
\pr. 8, 1925.

[6] RALSTON, O. C., G. S. TILLEY, U. S. Pat. 1,529,035, Mar. 10, 1925.

[7] FRISCHER, H., Ger. Pat. 317,633, Dec. 22, 1919.

reduces the iron in the aluminum sulfate solution with barium sulfide, metallic iron, or aluminum, and then uses barium dioxide or sodium peroxide to change the iron to an insoluble basic ferric compound.

A German patent[1] states that it is possible to increase the basicity of a basic aluminum salt solution without precipitating the alumina, provided a small amount of phosphoric acid is added.

Müller and Schlecht[2] claim that basic iron sulfate is precipitated from an aluminum sulfate solution after digesting for an hour at 180 to 200°C. This separation is based upon the fact that the ferric salt is hydrolyzed more rapidly and completely than the aluminum sulfate. Vittorf[3] describes a process in which hydrous aluminum sulfate is precipitated by means of 90 per cent alcohol from a mixture of aluminum and iron sulfates. After the third precipitation, little or no iron was found in the precipitate.

Clark[4] states that ferrous iron or arsenious acid in aluminum salt and other metallic salt solutions can be oxidized by injecting a mixture of nitric oxide and oxygen through a porous tube into the solution. The oxygen of the air is activated by the nitric oxide.

Precipitation of Alumina Leaving Iron and Other Impurities in Solution.

In the processes just described, the iron has been in the ferric state. If the iron is in the ferrous state, the order of precipitation is reversed and the alumina can be precipitated without precipitating the iron by making the solution slightly basic.

A process for the manufacture of basic aluminum sulfate containing little iron is described by Lindblad and Hultman.[5] The ferric compounds in the aluminum sulfate solution are first reduced to the ferrous state and then a salt, such as sodium chloride or sulfate, is added and the solution heated under pressure to precipitate the basic aluminum sulfate. The iron

[1] Schmatolla, O., Ger. Pat. 372,246, Mar. 26, 1923.

[2] Müller, C. and L. Schlecht, Ger. Pat. 448,848, Aug. 29, 1927.

[3] Vittorf, N., *Trans. Inst. Econ. Mineral. and Petr.* (Russia), **8**, 1-16, (1924).

[4] Clark, L. F., U. S. Pat. 1,649,152, Nov. 15, 1927.

[5] Lindblad, A. R., G. H. Hultman, Swed. Pats. 53,663, Feb. 7, 1923; 53,132, Dec. 6, 1922; Norw. Pat. 38,054, Oct. 15, 1923.

:mains in the solution as a ferrous salt. While the chloride ad sulfate give good results, other salts whose acid radicals irm soluble ferrous compounds may be used. Basic substances,[1] ich as alkali metal hydrate, carbonate, or ammonia, may be lded to help in the formation of the basic sulfate. Iron comounds may be removed from a basic sulfate[2] by heating with n acid or salt which forms soluble iron salts (such as hydrochloric cid or sodium chloride) provided the iron is first reduced to the irrous state.

Burkey and Schleicher[3] digest aluminum sulfate solutions ontaining an excess of potassium sulfate at pressures from 100 to 00 pounds in order to precipitate basic aluminum sulfate. he ferrous iron remains in solution, but the precipitate contains ime potassium sulfate.

According to Patrouilleau,[4] bauxite is dissolved in sulfuric cid and the iron salts reduced to the ferrous state. Ferrous xide is formed in the solution either by boiling with metallic on or by passing an electric current through the solution, sing an iron anode. The ferrous oxide supposedly forms a ulfate and, consequently, the alumina liberated forms basic ulfate. Upon dilution, the basic sulfate is precipitated in a ure state and is removed from the ferrous iron by filtering. later patent states that other metallic anodes may be used, or example, zinc and cadmium. In order to decrease the ost, certain substances, such as alkali or alkaline earth carbontes, may be added to increase the basicity of the solution. The itanium is precipitated as oxide and is removed from the basic luminum sulfate solution before it is diluted.

Hultman[5] adds calcium carbonate to an aluminum sulfate olution containing ferrous iron and obtains a precipitate of

[1] HULTMAN, G. H., A. R. LINDBLAD, Swed. Pat. 53,134, Dec. 6, 1922.

LEDERER, O., W. STANCZAK, and H. KASSLER, Br. Pat. 267,491, Nov. 24, 927; Fr. Pat. 630,569, Dec. 5, 1927.

SPENCE, H. and PETER SPENCE and SONS, LTD., Br. Pat 25,683 (1902), pplied for Nov. 22, 1902.

[2] LINDBLAD, A. R., G. H. HULTMAN, Swed. Pat. 53,133, Dec. 6, 1922.

[3] BURKEY, H. M., H. M. SCHLEICHER, U. S. Pat. 1,415,308, May 9, 1922.

[4] PATROUILLEAU, L. G., Br. Pat. 240,435, July 22, 1926; U. S. Pat. ,692,692, Nov. 20, 1928; Fr. Pats. 586,684, Apr. 1, 1925; 595,062, Sept. 25, 1925; Add. Pat. 30,170, Mar. 29, 1926; Swiss Pat. 118,226, Dec. 16, 1926.

[5] HULTMAN, G. H., U. S. Pat. 1,607,279, Nov. 16, 1926; Norw. Pat. 13,140, Oct. 11, 1926.

aluminum hydrate and calcium sulfate. He states that the iron remains in solution and that the calcium sulfate can be leached out of the alumina by means of water (!). After reducing the iron to the ferrous condition, Kessler[1] adds phosphoric acid before adding just enough soluble base to precipitate the alumina from an aluminum salt solution. According to a German patent,[2] basic aluminum sulfate is precipitated by ammonia, ammonium carbonate, alkali metal hydrate, carbonate, or sulfite from an aluminum salt solution after the iron is reduced to the ferrous state. The reaction should be carried out in a closed vessel, preferably in an atmosphere of carbon dioxide or sulfur dioxide.

According to Morel,[3] sodium thiosulfate precipitates alumina and sulfur from an aluminum sulfate solution, while ferrous iron remains in solution. The sulfur can be removed from the alumina by calcination or solution. Mejdell[4] states that alumina may be precipitated with sodium sulfide since the iron sulfide does not precipitate until all of the alumina is removed from solution. It is necessary to keep the iron in the ferrous condition and the precipitation is stopped upon the appearance of the black iron sulfide.

Pedemonte[5] treats an impure aluminum sulfate solution with aluminum or zinc until it no longer shows a red color with sulfocyanate. The alumina is precipitated by alkali carbonate, sulfate, or sulfite upon the application of heat, but the iron and titanium compounds remain in solution. Patrouilleau[6] treats an aluminum chloride or sulfate solution with sodium or potassium sulfite (3.7 to 4.65 mols sulfite to 1 mol Al_2O_3) after first reducing iron, etc., with metallic zinc or aluminum. Upon boiling, the alumina precipitates and the impurities supposedly remain in solution.

Bjorkstedt[7] uses ammonium sulfite (preferably containing an excess of sulfur dioxide) to precipitate a basic aluminum sulfite from which alumina is recovered by calcination.

[1] KESSLER, Fr. Pat. 244,304, Jan. 15, 1895; Br. Pat. 1419 (1895) Oct. 5, 1895.

[2] I. G. FARBENINDUSTRIE, A.-G., Ger. Pat. 429,717, June 1, 1926.

[3] MOREL, J., Br. Pat. 149,769, Aug. 17, 1920; Fr. Pat. 493,616, Aug. 14, 1919.

[4] MEJDELL, T. Norw. Pat. 28,991, Aug. 5, 1918.

[5] PEDEMONTE, A., Fr. Pat. 573,690, June 27, 1924; 1st Add. Pat. 28,083, Jan. 14, 1925; 2nd Add. Pat. 29,262, July 10, 1925.

[6] PATROUILLEAU, L. G., Fr. Pat. 567,456, Mar. 3, 1924.

[7] BJORKSTEDT, W. G., U. S. Pat. 1,681,921, Aug. 28, 1928.

urification by Crystallization of Aluminum Sulfate or an Alum.

Crystallization or recrystallization of aluminum sulphate
an alum reduces its iron content, and many inventors have
roposed variations of the conditions so as to make the elimina-
on of iron as complete as possible. Some prefer certain specific
ums, while others use aluminum sulphate. For either, a
rongly acid solution is recommended[1] to retain iron in solution.

If aluminum sulphate is to be crystallized out of a solution
ontaining iron, apparently the minimum amount of contami-
ation is obtained when the iron is present in the ferrous form.
his result may be obtained by reducing the iron in the solution
ith a metal, such as aluminum, zinc, or iron,[2] or oxalic acid or
xalates,[3] sulfites,[4] sulfides such as sodium, calcium,[5] zinc or
ad,[6] or by reducing the iron of the original mineral before
eatment with acid by heating it under reducing conditions.[7]
aureau[8] recommends the addition of a chloride, to leave iron
solution as ferric chloride.

The precipitation of hydrous aluminum chloride by means of
seous hydrochloric acid is said to eliminate the iron.[9]

A British patent[10] recommends that a boiling solution (1.39
ecific gravity) of aluminum sulfate be rapidly cooled by blowing
ith compressed air and the liquid removed from the magma
crystals in a centrifuge. Vacuum evaporation[11] is recom-
ended for aluminum sulfate solutions.

[1] CHEM. FAB. GRIESHEIM-ELEKTRON, Ger. Pat. 232,563, Mar. 17, 1911.

[2] GIRAUD, L., Fr. Pat. 585,984, Mar. 12, 1925.

[3] SEMPER, C., U. S. Pat. 238,613, Mar. 8, 1881.

[4] LA SOCIÉTÉ ANONYME DES ANCIENNES SALINES DOMANIALES DE L'EST,
. Pat. 1261 (1891), Nov. 28, 1891.

[5] ROBINSON, T., Br. Pat. 150 (1886), Jan. 5, 1886.

[6] PETRAEUS, C. V., U. S. Pat. 225,300, Mar. 9, 1880.

[7] MILBAUER, J., F. SKUTIL, *Chem. Ztg.*, **42**, 525 527 (1918).

[8] MAUREAU, A., Fr. Pat. 548,101, Jan. 5, 1923. See also NEWLANDS,
E. R., U. S. Pat. 243,949, July 5, 1881.

[9] ASSEEV, C., Br. Pat. 225,199, Oct. 15, 1925; Fr. Pat. 574,983, July 22,
24; Aust. Pat. 105,343, Jan. 25, 1927.

GARDAIR, F., T. GLADYSZ, U. S. Pat. 282,878, Aug. 7, 1883; Br. Pat.
30 (1882) Apr. 2, 1883.

[10] SPENCE, F. M., D. D. SPENCE, H. SPENCE, Br. Pat. 6254 (1900), Feb.
, 1901.

[11] SCOFIELD, S. W., J. B. LARUE, U. S. Pat. 1,503,603, Aug. 5, 1924.

BOCK, J., Ger. Pat. 131,314, May 26, 1902; Br. Pat. 9545 (1902), June
, 1902.

In crystallizing out potash alum, Laist, Frick and Oliver[1] first reduce the iron in solution to the ferrous state, while Pedersen[2] claims that most of the iron present in air-dried clay is already in the ferrous state and that the ferric iron is either not dissolved or else reprecipitated by an excess of clay. Thus he crystallizes potash alum from the solution containing iron in the ferrous state. Moxham[3] proposes to recover the aluminum in sulfuric acid solutions of iron ores by adding potassium sulfate and crystallizing out the potash alum. Javet[4] adds the calculated amount of sodium or potassium salt and sulfuric acid to clay in order to form alum. The silica is removed by decantation or other means and the solution cooled so that the alum can crystallize from solution.

Soda alum is much more soluble than potash alum, and it appears to be difficult to crystallize it at all, although it is claimed[5] that when it is crystallized from a solution containing an excess of sodium sulfate, preferably slightly acid,[6] by agitation at temperatures of 25 to 50°C., the iron remains in solution. Augé,[7] on the contrary, in order to form crystals, states that the solution should contain an excess of aluminum sulfate and should be between 10 and 25°C., since above 25°C. the crystals form very slowly, and below 10°C. they contain an excess of sodium sulfate. The density of the solution should not be over 1.35 at 50°C., or else the crystals will come down in mushy form. If obtained,[8] this crystal mush may be spread in layers about

[1] LAIST, F., F. F. FRICK, R. S. OLIVER, U. S. Pats. 1,300,117 and 1,300,118, Apr. 15, 1919.

[2] PEDERSEN, H., U. S. Pat. 1,406,890, Feb. 14, 1922; Br. Pat. 169,301, Sept. 29, 1921; Fr. Pat. 518,331, May 23, 1921; Ger. Pat. 380,234, Sept. 5, 1923; Swed. Pat. 52,943, Nov. 1, 1922; Norw. Pat. 35,193, July 3, 1922. *Tids. Kemi Bergvesen* **3**, 161-4, 175-8 (1923); **4**, 11-17 (1924); *Teknisk Ukeblad* **42**, 75-7, 83-6 (1924).

[3] MOXHAM, A. J., U. S. Pats. 1,538,838 and 1,538,840, May 19, 1925. *Iron Age* **113**, 1637–1639 (1924).

[4] JAVET, E., Fr. Pat. 586,115, Mar. 16, 1925.

[5] STROHBACH, E., U. S. Pat. 932,067, Aug. 24, 1909; Br. Pat. 28,581 (1906) Oct. 3, 1907; Fr. Pat. 372,809, Apr. 19, 1907; Norw. Pat. 16,536, July 8, 1907; Swed. Pat. 23,405, Nov. 9, 1907.

[6] KAUFFMANN, O., Ger. Pat. 216,034, Nov. 6, 1909.

[7] AUGÉ, E., Ger. Pats. 50,323, Jan. 28, 1890; 52,836, July 3, 1890. See also Br. Pat. 11,975 (1889), June 28, 1890.

[8] AUGÉ, E., Ger. Pats. 53,570, Aug. 26, 1890; 55,419, Jan. 22, 1891. See also Br. Pat. 16,711 (1889), Mar. 8, 1890.

inches deep and allowed to recrystallize at 10 to 25°C. Others[1] recommend neutral or slightly basic solutions, with a density of 1.38 to 1.45. Harrison and Semper[2] agree with Augé in preferring a solution having an excess of aluminum sulfate. By mixing saturated solutions of sodium sulfate and aluminum sulfate, both containing separated crystals, a crop of well-defined soda alum crystals is said to form.[3] Good crystals of soda alum[4] can also be produced by mixing a hot saturated solution of soda alum with a cold saturated solution. It is claimed[5] that seeding a soda alum solution with crystals avoids the formation of anhydrous salt and produces a product with less iron.

Ammonia alum is preferred by some[6] for a separation by recrystallization, particularly in the presence of ferric iron,[7] although Larson and Bergman[8] reduce the iron to the ferrous state by the addition of a sulfite before the crystallization, and Pedemonte[9] also prefers to have the iron in the ferrous state. Janssen[10] adds an excess of ammonium sulfate and then enough ammonia to form a basic ferric salt, which is alleged to have less tendency than the normal salt to contaminate the alum crystals. Heating this basic solution at 75 to 80°C. for 1 hour and cooling with agitation are prescribed for decreasing the amount of iron in the final product.

[1] DUMONT, G., Ger. Pat. 141,670, May 9, 1903.
    BOCK, J., Ger. Pat. 178,236, Nov. 8, 1906.
[2] HARRISON, T. S. and C. SEMPER, U. S. Pats. 497,570; 497,571, May 16, 1893.
[3] SPENCE, F. M., D. D. SPENCE, H. SPENCE, Br. Pat. 5,644 (1900), Feb. 1, 1901.
[4] SPENCE, F. M., D. D. SPENCE, Br. Pat. 17,888 (1889), Oct. 18, 1890.
[5] KESSLER, J. L., Br. Pat. 2,710 (1893), Dec. 2, 1893.
[6] BUCHNER, M., Ger. Pat. 388,168, Jan. 10, 1924.
    SPENCE, H., Br. Pat. 25,683 (1902), applied for Nov. 22, 1902.
    HELLSING, G. H., Swed. Pat. 20,927, May 26, 1906.
    RINMAN, E. L., Swed. Pat. 62,272, Jan. 25, 1927.
    ZABICKI, S., *Przemysl Chem.* **12**, 77–90 (1928).
[7] BARNETT, M., L. BURGESS, U. S. Pat. 1,280,636, Oct. 8, 1918.
[8] LARSON, J. P. A., W. D. BERGMAN, Br. Pat. 120,550, Mar. 20, 1919; Norw. Pat. 32,204, Apr. 25, 1921; Swed. Pat. 50,799, Feb. 1, 1922.
[9] PEDEMONTE, A., Fr. Pat. 577,671, Sept. 9, 1924.
[10] GANSSEN, R., U. S. Pat. 1,619,666, Mar. 1, 1927; R. GANS, Br. Pat. 132,510, Dec. 8, 1920; Fr. Pat. 519,526, June 11, 1921; Swiss Pat. 90,697, Sept. 16, 1921; Norw. Pat. 32,548, June 27, 1921; Swed. Pat. 52,575, Aug 30, 1922. See also J. D. RIEDEL A.-G., Ger. Pat. 368,650, Feb. 9, 1923; 375,703, May 17, 1923; 424,701, Jan. 29, 1926.

Electrochemical Removal of Iron.

Various inventors have proposed an electrolytic separation of iron and aluminum in aqueous solutions. One[1] proposes to deposit metallic iron in a mercury cathode, while another[2] claims the same result without the use of mercury. A much later inventor[3] agitates with air during electrolysis of a sulfuric acid solution, and precipitates the iron as ferric hydroxide at the cathode. Patrouilleau[4] claims that a short-circuited voltaic couple of iron and copper in a hot solution of aluminum sulfate reduces the iron to the ferrous form and increases the basicity of the aluminum sulfate so that upon dilution the latter will be precipitated. Electrolysis of impure aluminum sulfate solutions with anodes of iron, nickel, cobalt, cadmium, or zinc is said to work in a similar manner.[5] The addition of alkalies or alkaline earth oxides or carbonates increases the basicity of the solution and consequently decreases the current consumption. While Giordani[6] states that aluminum-carbon voltaic couples will precipitate the iron from neutral solutions of aluminum salts, Sem[7] states that ferrous solutions will not precipitate at the cathode as long as an excess of an aluminum salt is present. If a sulfate is used, basic aluminum sulfate will be precipitated. Boulton[8] uses a combined magnetic-electrolytic treatment to remove iron from aluminum sulfate solutions at 100°F. Morris[9] uses an electrolytic cell with a diaphragm, placing the aluminum salt solution in the anode compartment and an alkali chloride in the cathode compartment. Upon electrolysis, alumina is said

[1] VON KLOBUKOW, N., Ger. Pat. 53,392, Sept. 18, 1890. See also WASILEWSKI, L., S. MANTEL, *Przemysl Chem.* **12**, 48-52 (1928).

[2] LOEWIG AND Co., Br. Pat. 2,506 (1883), applied for May 19, 1883; Ger. Pat. 25,777, Jan. 10, 1884.

[3] McKEE, R. H., U. S. Pat. 1,290,269, Jan. 7, 1919.

[4] PATROUILLEAU, L. G., Fr. Pat. 627,334, Oct. 1, 1927.

[5] PATROUILLEAU, L. G., Br. Pat. 240,435, July 22, 1926; Fr. Pats. 586,684, Apr. 1, 1925; Add. Pat. 30,170, Mar. 29, 1926; 595,062, Sept. 25, 1925; Swiss Pat. 118,226, Dec. 16, 1926.

[6] GIORDANI, F., Fr. Pat. 540,715, July 17, 1922; U. S. Pat. 1,685,156, Sept. 25, 1928.

[7] SEM, M. O., U. S. Pat. 1,382,808, June 28, 1921; Norw, Pat. 30,115, Oct. 20, 1919.

[8] BOULTON, J., Br. Pat. 20,227 (1914), July 29, 1915.

[9] MORRIS, F. W., U. S. Pat. 890,084, June 9, 1908; Br. Pat. 6,449 (1908), Mar. 11, 1909; Can. Pat. 105,821, June 11, 1907; Fr. Pat. 391,398, Oct. 30, 1908. See also HIROTA, R., Jap. Pat. 30,130, Oct. 5, 1916; *C. A.* **11**, 1604, (1917).

to migrate to the cathode compartment, forming alkali aluminate, while chlorine and sulfuric acid are formed at the anode. This seems the least practical of any of the proposed electrolytic separations.

Thermal Processes for Separation of Iron.

Certain thermal processes aid in the separation of iron oxide and alumina. For instance, a partial calcination[1] of the iron-bearing sulfate is said to decompose the iron sulfate, whereas the aluminum sulfate does not decompose and can be removed by leaching. Moxham[2] states that anhydrous iron sulfate dissolves more rapidly in water than anhydrous aluminum sulfate, and suggests that a mixture of the two salts might be separated by leaching. According to Hurter,[3] the aluminum sulfate is heated to a dark-red heat in the presence of reducing gases; the iron can then be dissolved in dilute hydrochloric acid. If a chloride is present during the heating, the iron is volatilized as the chloride. Jacobsson[4] treats a porous mixture of alumina and iron oxide with reducing gases and then with dry chlorine (or hydrochloric acid) in the presence of aluminum chloride (also carbon, chromium, or tin chlorides) at a temperature of 300°C. to form volatile iron chloride. Air or moisture should be absent, but the use of aluminum chloride makes it possible to work in the presence of traces of these undesirable constituents. Foreign patents of recent date[5] state that after the aluminum salt has been heated to form the oxide, the iron impurities may be removed as the metal by fusing with a reducing agent.

[1] NORSK ALUMINIUM Co., Norw. Pat. 32,490, June 20, 1921.

HULTMAN, G. H., Swed. Pat. 55,702, Dec. 11, 1923.

HART, E., U. S. Pat. 1,322,900, Nov. 25, 1919.

[2] MOXHAM, A. J., U. S. Pat. 1,489,362, Apr. 8, 1924; Fr. Pat. 558,159, Aug. 23, 1923.

[3] HURTER, A., Br. Pat. 203,798, Sept. 17, 1923.

[4] JACOBSSON, R., U. S. Pat. 1,570,353, Jan. 19, 1926; Br. Pats. 221,209, Aug. 6, 1925; 243,183, Nov. 26, 1925; Fr. Pat. 584,901, Feb. 18, 1925; Swiss Pat. 117,772, Dec. 1, 1926; Aust. Pat. 105,338, Jan. 25, 1927; Norw. Pat. 44,025, May 25, 1927.

[5] I. G. FARBENINDUSTRIE, A.-G., Br. Pat. 272,748, June 23, 1927; Norw. Pat. 45,611, Oct. 1, 1928; Aust. Pat. 110,855, Oct. 10, 1928; Can. Pat. 276,643, Dec. 20, 1927.

Miscellaneous Methods.

According to Goldschmidt,[1] the minerals rich in plagioclases are easily decomposed with dilute acids. The iron content of the labradorite anorthosite rocks is not easily dissolved by dilute acids, so alumina free of iron may be obtained from them. A German patent[2] states that the proportion of iron dissolved in the treatment of clay with ammonium sulfate can be considerably reduced by working at a lower temperature and for a shorter time than is required to give the maximum yield of alumina.

Starting with a mixture of aluminum hydrate and ferrous sulfide, Pezzolato and de Felice[3] convert the alumina into soluble sodium aluminate by the action of sodium sulfide and supposedly filter off the insoluble iron sulfide. In several patents, Buchner[4] describes the separation of a mixture of aluminum and iron hydroxides obtained in the acid process by treating them with sodium hydroxide. Moxham[5] heats the mixture of iron and aluminum oxides, obtained from the calcination of the sulfates, with soda and recovers the alumina as soluble alkali aluminate. In the German patents to Chemische Fabrik Griesheim-Elektron,[6] the clay is first decomposed with hydrochloric or sulfuric acid and then heated at 300 to 600°C. in the presence of steam. The resulting product consists of a mechanical mixture of silica and alumina, which may be separated by electroösmosis, or by means of sodium hydroxide, which dissolves the alumina, but is said to dissolve very little of the silica and none of the iron. Doelter,[7] Pedemonte,[8] and Rosen-

[1] Goldschmidt, V. M., U. S. Pat. 1,380,552, June 7, 1921; Br. Pat. 112,948, June 20, 1918; Ger. Pat. 365,348, Dec. 13, 1922; Norw. Pats. 28,656, Dec. 30, 1918; 30,824, June 21, 1920; Swed. Pat. 50,845, Feb. 8, 1922.

[2] J. D. Riedel A.-G., Ger. Pat. 359,975, Sept. 28, 1922.

[3] Pezzolato, A., M. T. de Felice, Fr. Pat. 364,265, Aug. 18, 1906; Br. Pat. 6,122 (1906) June 21, 1906.

[4] Buchner, M., U. S. Pat. 1,162,130, Nov. 30, 1915; Br. Pat. 15,854 (1914), applied for July 2, 1914; Fr. Pat. 477,925, Nov. 17, 1915; Ger. Pat. 229,121, Feb. 26, 1921; Swiss Pat. 87,751, Jan. 3, 1921; Swed. Pat. 47,699, Sept. 8, 1920.

[5] Moxham, A. J., Fr. Pat. 558,159, Aug. 23, 1923; Br. Pat. 211,536, Feb. 25, 1924.

[6] Ger. Pats. 369,233, Feb. 16, 1923; 411,580, Apr. 2, 1925.

[7] Doelter, C., Ger. Pat. 65,085 Oct. 12, 1892.

[8] Pedemonte, A., U. S. Pat. 1,490,021, Apr. 8, 1924; Br. Pat. 195,295, Mar. 29, 1923; Fr. Pat. 547,862, Dec. 27, 1922; Add. Pat. 26,369; Swiss Pat. 101,612, Oct. 1, 1923.

thal[1] suggest the removal of the magnetic impurities in alumina by means of a magnetic separator. Pedemonte[2] calcines bauxite at a dull red heat after removing the iron with dilute acid. The silica and titanic acid are insoluble in fuming hydrochloric acid, while the alumina is soluble. In preparing aluminum sulfate for the manufacture of paper, Lienau[3] reduces the iron in an aluminum sulfate solution with hydrogen sulfide. The free acid is neutralized with magnesia and the double salt which is formed with the ferrous iron and magnesium sulfate is colorless and not affected by light.

An early British patent to Le Chatelier[4] describes various methods for preparing alumina from aluminum sulfate by heating with magnesium or barium compounds, sodium chloride, soda ash, sodium nitrate, or sodium sulfate, and carbon.

PRODUCTION OF ALUMINA FROM SALTS OF ALUMINUM

Precipitation of Alumina by Ammonia.

If alumina be precipitated from an aluminum salt solution, by the addition of ammonia, as recommended by many patentees, the resulting highly hydrated precipitate tends to be colloidal, very voluminous, and very difficult to filter and wash. X-ray spectrographs show that this is not the trihydrate $Al_2O_3.3H_2O$ which is precipitated in the Bayer process, but apparently a different form. This precipitate has a strong tendency to either adsorb salts or include basic aluminum salts, which resist solution in water. Some inventors prefer to remove the sulfate radical from aluminum sulfate or alum solutions before attempting to precipitate the alumina. This is usually accomplished by adding a calcium or barium compound and filtering off the insoluble sulfate.[5]

[1] ROSENTHAL, G., Br. Pat. 6,290 (1884), applied for Apr. 12, 1884; Ger. Pat. 31,357, May 9, 1885.

[2] PEDEMONTE, A., U. S. Pat. 1,490,021, Apr. 8, 1924; Fr. Add. Pat. 25,538, Mar. 19, 1923.

[3] LIENAU, F., Ger. Pats. 21,346, Feb. 22, 1883; 23,193, Aug. 10, 1883.

[4] LE CHATELIER, L., Br. Pat. 2,654 (1860), applied for Apr. 30, 1861.

[5] SOCIETÀ ROMANA SOLFATI. Br. Pat. 6,180 (1903), applied for Mar. 17, 1903.

YNGSTRÖM, L. and A. R. LINDBLAD, Swed. Pat. 41,110, Aug. 9, 1916.

EUSTIS, F. A., U. S. Pat. 1,377,882, May 10, 1921.

HAYWARD, C. R., H. M. SCHLEICHER, F. O. STILLMAN, U. S. Pat. 1,370,646, Mar. 8, 1921.

In order to get a precipitate which may be readily filtered and washed, it has been proposed[1] to heat the precipitated mixture in an autoclave for several hours, or[2] to carry on the precipitation in a digester under pressure of 10 to 15 atmospheres, or[3] to boil a basic aluminum sulfate with ammonia under pressure. Blanc[4] adds ammonia, preferably gaseous, to a boiling and violently agitated aluminum sulfate solution. The Riedel Company[5] saturates a strong ammonia solution with ammonium sulfate before adding it to the aluminum sulfate solution.

Heibling,[6] Buchner,[7] and Yamazaki and Yasuda[8] pass ammonia gas over moist solid crystals of alum or aluminum sulfate. Darling[9] recommends the use of a concentrated aluminum salt solution, while Langlet and Rinman[10] add droplets of such a solution, or the powdered aluminum salt to the solution of the alkali. This idea has been elaborated by Buchner[11] and his collaborators, who use a large excess of concentrated ammonia

[1] HALVORSEN, B. F., U. S. Pat. 1,333,020, Mar. 9, 1920; Fr. Pat. 505,270, July 27, 1920.

[2] NORSK HYDRO-ELEK. KVAEL., Br. Pat. 134,531, July 8, 1920.

[3] HULTMAN, G. H., Swed. Pat. 57,812, Nov. 11, 1924.

[4] BLANC, G. A., Br. Pat. 181,678 (Void), applied for Feb. 15, 1922.

[5] J. D. RIEDEL A.-G., Ger. Pat. 442,255, Mar. 24, 1927.

[6] HEIBLING, J., U. S. Pat. 521,712, June 19, 1894; Fr. Pat. 227,425, Jan. 25, 1893; Add. Pat. July 12, 1894; Ger. Pat. 70,549, July 26, 1893.

[7] BUCHNER, M., U. S. Pat. 1,337,191, Apr. 20, 1920; Ger. Pat. 301,612, Aug. 3, 1921.

[8] YAMAZAKI, Z., and M. YASUDA, Jap. Pat. 44,219 (1922).

YAMAZAKI, Z., *J. Soc. Chem. Ind.* (Japan), **29**, 154-60 (1926.)

[9] DARLING, J. D., U. S. Pat. 285,579, Sept. 25, 1883; Br. Pat. 1,577 (1883) Sept. 27, 1883; Ger. Pat. 26,705, Mar. 24, 1884.

[10] LANGLET, N. A., E. L. RINMAN, U. S. Pat. 1,015,499, Jan. 23, 1912; Br. Pat. 17,589 (1908), Mar. 25, 1909; Fr. Pat. 388,527, Aug. 14, 1908; Ger. Pat. 201,893, Sept. 18, 1908; Norw. Pat. 19,654, Jan. 31, 1910.

[11] BUCHNER, M., U. S. Pats. 1,337,192, Apr. 20, 1920; 1,386,920, Aug. 9, 1921; 1,493,320, May 6, 1924; Br. Pats. 16,597 (1915), Apr. 7, 1921; 162,303, May 5, 1921; 195,998, Apr. 12, 1923; Fr. Pats. 505,532, July 31, 1920; 511,809, Jan. 5, 1921; 515,062, Mar. 24, 1921; 542,176, Aug. 7, 1922; Ger. Pats. 301,675, Jan. 12, 1921; 303,923, Mar. 22, 1921; Add. Pat. 302,412, July 8, 1921; 348,905, Feb. 18, 1922; 425,222, Feb. 13, 1926; Swiss Pats. 84,909, Apr. 16, 1920; 86,189, Aug. 2, 1920; Swed. Pats. 46,112, Nov. 26, 1919; 53,945, May 9, 1923; 51,345, Apr. 5, 1922; Norw. Pat. 40,118, Nov. 3, 1924; Aust. Pat. 106,692, June 25, 1927.

BUCHNER, M., Ger. Pat. 388,168, Jan. 10, 1924; Norw. Pat. 35,803, Oct. 2, 1922; Swed. Pat. 51,345, Apr. 5, 1922.

J. D. RIEDEL A.-G., Ger. Pat. 424,701, Jan. 29, 1926.

solution, to which is added either a very concentrated aluminum sulfate solution (preferably in droplets) or small crystals of aluminum sulfate. In the latter case, the precipitated hydrate forms pseudomorphs of the crystals, which are strong enough to stand careful handling and may be satisfactorily filtered and washed. This has been demonstrated in semi-commercial experiments. The sulfate may be converted to chloride before precipitation if desired.[1]

Other Precipitating Agents.

Ammonium carbonate,[2] sodium carbonate,[3,4] milk of lime,[5] calcium carbonate,[6,7] magnesia or baryta[8] and alkali sulfide[9,10] have been proposed for precipitating aluminum salt solutions. Aluminum and iron may be precipitated together by potassium sulfide[11] or sodium sulphydrate,[12] and then separated by transforming the alumina into soluble aluminate by means of sodium sulfide and precipitating the alumina by means of hydrogen sulfide. It is also claimed[13] that iron filings will precipitate alumina from a hot (90°C.) aluminum sulfate solution, leaving the iron in the solution. Colloidal matter may be removed[14] from an aluminum sulfate solution by means of "packing-house stick," or a slowly precipitating arsenic sulfide.[15]

[1] BUCHNER, M., Fr. Pat. 505,232, July 26, 1920; Ger. Pat. 299,781, July 7, 1921.

[2] SOCIETÀ ROMANA SOLFATI, Br. Pat. 3,776 (1904), applied for Feb. 15, 1904.

[3] PEDEMONTE, A., U. S. Pat. 1,490,021, Apr. 8, 1924.

[4] BAN, T., T. TIKUCHI, Jap. Pat. 31,720; (C. A. 12, 1238).

[5] ROTHBERG, M. E., U. S. Pat. 657,453, Sept. 4, 1900. ALVISI, U., and F. MILLOSEVICH, Br. Pat. 8,302 (1902), Apr. 9, 1903.

[6] SOCIETÀ ROMANA SOLFATI, Fr. Pat. 330,280, Aug. 17, 1903.

[7] PEDEMONTE, A., Fr. Pat. 577,671, Sept. 9, 1924.

[8] EUSTIS, F. A., U. S. Pat. 1,212,334, Jan. 16, 1917.

[9] LE CHATELIER, L., Br. Pat. 2,654 (1860), filed Apr. 30, 1861.

[10] NORSKE AKTIESELSKAB FOR ELEKTROKEMISK INDUSTRI, Norw. Pat. 28,991; Aug. 5, 1918.

[11] PEZZOLATO, A., M. T., DE FELICE, Fr. Pat. 364,265, Aug. 18, 1906; Br. Pat. 6,122 (1906) June 21, 1906.

[12] RINMAN, E. L., Br. Pat. 243,356, Nov. 25, 1926; Swed. Pat. 62,273, Jan. 25, 1927.

[13] MOXHAM, A. J., U. S. Pat. 1,538,839, May 19, 1925.

[14] DEANE, W. A., U. S. Pat. 1,359,037, Nov. 16, 1920.

[15] SPENCE, H. and P. SPENCE and SONS, LTD., Br. Pat. 6,529 (1906) Mar. 14, 1907.

Sulfite solutions of alumina may be precipitated by merely boiling off the excess of sulfur dioxide.[1] A fractional precipitation of this type, to separate alumina from dissolved silica has been described,[2] but laboratory tests indicate that it is unsatisfactory.

Alumina Production by Calcination of the Sulfate.

Both the simple sulfate and the alums crystallize with large amounts of water of crystallization. The calcination process, therefore, consists of two steps: first, removal of crystal water, and second, decomposition of the anhydrous salts to form alumina, oxygen, and oxides of sulfur. The drying process takes place at relatively low temperatures (apparently 180 to 300°C.), while the decomposition of the anhydrous salt begins at higher temperatures and probably requires about 900°C. or higher for its completion.

Difficulties arise in the drying step because of the tendency of the salts to melt in their water of crystallization if the temperature is raised too rapidly, or to form dried crusts which impede the passage of both heat and moisture. Some inventors[3] recommend a very gradual increase in temperature during the drying period, while others[4] go to the other extreme and heat the salt very rapidly indeed.

[1] COMPAGNIE GÉNÉRALE L'ALUMINE SOCIÉTÉ ANONYME, Norw. Pat. 7,552, Sept. 4, 1899; Dan. Pat. 2,340, July 3, 1889.

RAMSAY, J. H., F. R. LOWE, Br. Pat. 9,705, Aug. 3, 1916.

RAYNAUD, E., U. S. Pat. 650,753, May 29, 1900; Ger. Pat. 107,502, Nov. 14, 1899; Swed. Pat. 10,268, Oct. 14, 1899.

WILDMAN, H. G., U. S. Pat. 1,326,384, Dec. 30, 1919; Br. Pat. 161,310, Apr. 14, 1921; Fr. Pat. 509,142, Nov. 2, 1920; *Quarry, Surveyors and Contractors' J.*, **27**, 233 (1922).

YNGSTRÖM, L., A. R. LINDBLAD, S. A. J. BERGSCHÖLD, Swed. Pat. 40,757, June 7, 1916.

[2] KALMUS, H. T., W. L. SAVELL, U. S. Pats. 1,090,479, Mar. 17, 1914; 1,148,092, July 27, 1915.

[3] PERRY, R. S., H. G. SCHANCHE, U. S. Pat. 748,525, Dec. 29, 1903.

CUMMER, A. E., U. S. Pat. 769,534, Sept. 6, 1904; Fr. Pat 330,055, Aug. 11, 1903; Br. Pat. 4,820 (1903), June 18, 1903.

HIROTA, K., Jap. Pat. 30,654, Jan. 23, 1917; *C. A.* **11**, 2392 (1917).

[4] PEDERSEN, H., U. S. Pat. 1,406,890, Feb. 14, 1922; Br. Pat. 169,301, Sept. 29, 1924; Ger. Pat. 380,234, Sept. 5, 1923; Fr. Pat. 518,331, May 23, 1921; Swed. Pat. 52,943, Nov. 1, 1922.

WANG, E., Norw. Pat. 36,038, Oct. 23, 1922.

Tilley[1] heats potash alum at 80 to 85°C. for several hours in a current of air or other inert gas to eliminate more than one-half the water of crystallization. After this preliminary heating, the crystals do not melt when heated at 800 or 1000°C. to drive off the sulfur trioxide.

Barnett and Burgess[2] proceed gradually from the solution to the molten hydrated salt by increasing the temperature with continual vigorous stirring, and continue the heating and stirring until the salt is dry. To produce a porous mass, Enequist[3] has suggested that the solution may be concentrated until it starts to solidify, and then poured out on sheet zinc or aluminum, so that the evolved hydrogen passes through the cooling mass.

Jacobsson[4] recommends vacuum drying to produce porous lumps, or the formation of small lumps by blowing the hot saturated solution with air. Howard[5] dries on a heated revolving plate, to which liquid is fed and from which the solid is scraped off. Llewellyn[6] dries the aluminum sulfate in a very similar manner by distributing the hot saturated solution of the salt in a thin film upon the surface of a revolving drum or cylinder.

Reducing agents, such as pitch,[7] carbon,[8,9] or sulfur[10] may be added to facilitate the decomposition of the anhydrous salt in the second step. Steam[11] and reducing gases[12] also may be used

[1] TILLEY, G. S., U. S. Pat. 1,686,112, Oct. 2, 1928.

[2] BARNETT, M., L. BURGESS, U. S. Pats. 1,252,384; 1,252,648, Jan. 8, 1918.

[3] ENEQUIST, J., U. S. Pat. 520,416, May 29, 1894.

[4] JACOBSSON, R., U. S. Pat. 1,570,353, Jan. 19, 1926; Br. Pats. 221,209, Aug. 6, 1925; 243,183, Nov. 26, 1925; Fr. Pat. 584,901, Feb. 18, 1925; Swiss Pat. 117,772, Dec. 1, 1926; Norw. Pat. 44,025, May 25, 1927; Aust. Pat. 105,338, Jan. 25, 1927.

[5] HOWARD, H., U. S. Pat. 1,173,428, Feb. 29, 1916.

[6] LLEWELLYN, I. P., Br. Pat. 26,616 (1912), Sept. 25, 1913.

[7] WEBSTER, J., U. S. Pat. 252,982, Jan. 31, 1882; Br. Pat. 2,580 (1881), filed Dec. 14, 1881; Ger. Pat. 18,721, July 4, 1882.

[8] EMANUEL, P. A., U. S. Pat. 957,848; May 10, 1910; Br. Pat. 20,048 (1910) (Void).

LAGE, Fr. Pat. 419,169, Dec. 28, 1910; Can. Pat. 129,195; Nov. 15, 1910.
SCHWAHN, H. F. D., U. S. Pat. 1,171,360, Feb. 8, 1916.

[9] TANAHASHI, T., Jap. Pat. 30,706, Jan. 31, 1917; C. A. 11, 2,393, (1917).

[10] EMANUEL, P. A., U S. Pat. 455,611, July 7, 1891.

[11] BLACKMORE, H. S., U. S. Pat. 724,251, Mar. 31, 1903.

HEWITT, J. T., F. G. POPE, Br. Pat. 14,911 (1898), May 13, 1899.
SCHWAHN, G., U. S. Pats. 1,132,737; 1,132,736, Mar. 23, 1915.

[12] ASKENASY, P., M. DREIFUSS, Ger. Pats. 383,434, Oct. 13, 1923; 406,063, Nov. 13, 1924.

to assist in the decomposition. When steam is to be used, some inventors prefer to add magnesium chloride with or without a little lime[1] or alkali chlorides,[2] especially sodium chloride[3] When aluminum sulfate is moderately heated with the correct amounts of sodium chloride, carbon, and moisture, hydrochloric acid is evolved and upon heating to a higher temperature, sodium aluminate is formed.[4] Herrenschmidt[5] melts a mixture of aluminum sulfate, boric acid, and zinc sulfate in the electric furnace to obtain fused alumina. The zinc sulfate is added to prevent the formation of carbides at the electrodes and the boric acid to act as a solvent and aid in the fusion. Froelich[6] prepares molten alumina by heating aluminum sulfate under pressure. The dissolved gases (sulfur trioxide and water) are removed upon releasing the pressure and the alumina remains behind.

ALUMINA FROM ALUNITE

Alunite is a naturally occurring basic sulfate of aluminum and potassium of the approximate composition, $K_2O.3Al_2O_3.4SO_3.6H_2O$, or as it is sometimes written, $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$. According to Mitscherlich,[7] this compound may be prepared artificially by adding an alkali to a solution of alum until the further addition would produce a permanent precipitate, and then heating the resultant solution of "neutral" alum in a sealed tube at 40°C. until the artificial alunite is precipitated. The crystalline form may be prepared by heating the neutral alum in a sealed tube at 230°C. The natural product is insoluble, or only very slightly soluble in water. Its greatest handicap is the inaccessibility of the deposits.

[1] ROSENTHAL, G., Br. Pat. 6,290 (1884), applied for Apr. 12, 1884; Ger. Pat. 31,357, May 9, 1885.

[2] HUMPHREY, C. W., U. S. Pat. 1,546,290, July 14, 1925.

[3] KEOGH, L. R., U. S. Pats. 740,364, Sept. 29, 1903; 744,765, Nov. 24, 1903; 794,413, July 11, 1905; Br. Pats. 23,918 (1903), Feb. 25, 1904; 23,919 (1903) Jan. 14, 1904; 2,655 (1904), Oct. 20, 1904.

[4] GAREAU, N. J., Fr. Pat. 639,844, June 30, 1928.
I. G. FARBENINDUSTRIE, A.-G., Br. Pat. 300,184, Nov. 5, 1928; Can. Pat. 279,990, May 8, 1928; Fr. Pat. 639,177, June 15, 1928

[5] HERRENSCHMIDT, H., Br. Pat. 2,678 (1908), Sept. 17, 1908; Swiss Pat. 43,906, Feb. 6, 1908.

[6] FROELICH, F., Swiss Pat. 125,709, May 1, 1928.

[7] MITSCHERLICH, A., *J. prakt. Chem.*, **81**, 108 (1860); **83**, 464 (1861).

Various methods have been suggested for the production of potash and alumina from this ore and they may be roughly divided into two classes; those in which sulfuric acid is added to the substance, and those in which the combined sulfate is partly or totally decomposed.

Concentration by Density or Flotation Methods.

Hagedorn[1] roasts the crushed ore to decompose the aluminum sulfate and hence decrease the density of the alunite. The density of the gangue does not change appreciably, and therefore the alumina and gangue may be separated by gravity methods after the soluble potassium sulfate is removed. According to Hornsey,[2] a flotation method may be used to separate the alumina from the impurities in roasted alunite after the soluble products have been removed. About 2 pounds of oleic acid per ton of impure alumina are required to effect the separation.

Digestion with Acids and Other Substances.

Tilley[3] digests pulverized alunite with 20 per cent sulfuric acid at 90°C. for 24 to 48 hours in order to remove practically all the iron and potassium and a part of the aluminum as sulfates. After reducing the iron to the ferrous state, the potash is crystallized from the solution as alum, leaving some aluminum sulfate still in solution. The residue which did not dissolve in the sulfuric acid is practically free from iron and after roasting can be dissolved in dilute sulfuric acid to form pure aluminum sulfate.

Moldenke[4] digests pulverized alunite with concentrated sulfuric acid at its boiling point in a closed vessel and then leaches out the sulfates to recover them by crystallization. Calcination is carried out in steps in a circulating atmosphere of sulphur dioxide and oxygen, whereby first the iron, and then the aluminum sulfates are decomposed, while the potassium sulfate remains unchanged. Cameron and Cullen[5] heat a mixture of pulverized alunite and 50° Bé. sulfuric acid at 150 to 200°C. After adding a 10 per cent excess of water above that required to furnish 24 mols of water for the alum and 18 mols for the aluminum sulfate, the solution is filtered and the alum allowed to crystallize. The aluminum sulfate which still remains in solution is recovered by evaporating the excess water.

[1] HAGEDORN, G. F., U. S. Pats. 1,253,590; 1,253,591, Jan. 15, 1918.

[2] HORNSEY, J. W., U. S. Pat. 1,255,749, Feb. 5, 1918; Br. Pat. 118,063, Aug. 15, 1918; Norw. Pat. 29,699, May 5, 1919; Swed. Pat. 17,157, June 16, 1920.

[3] TILLEY, G. S., U. S. Pat. 1,591,798, July 6, 1926.

[4] MOLDENKE, R., U. S. Pat. 1,282,273, Oct. 22, 1918.

[5] CAMERON, F. K., J. A. CULLEN, U. S. Pat. 1,239,768, Sept. 11, 1917.

Chappell[1] treats crushed alunite with sulfuric acid and then after filtering, precipitates the iron with ferrocyanide. The alumina is then precipitated with ammonia and the mixed sulfates of potassium and ammonium recovered for use as fertilizer.

In the patent to Detwiller,[2] the finely powdered alunite is digested under constant agitation with boiling nitric acid. The silica is insoluble, while potassium and alumina go into solution as nitrates and sulfates. The alumina is precipitated with ammonia or caustic potash while the solution is constantly agitated.

In a French patent,[3] the alunite is boiled with calcium hydroxide or carbonate and the resulting solution of potassium sulfate filtered off and the salt recovered by crystallization. The alumina is recovered from the residue by digesting with hot sodium hydroxide solution.

Meyers[4] passes sulfur dioxide and oxygen over alunite heated to a temperature of about 450 to 550°C., thus forming sulfur trioxide, which neutralizes the basic part of the compound.

Furnace Processes.

These are inherently unsatisfactory because of the difficulty in controlling the temperature throughout the heated mass. According to Bowley,[5] alunite is completely decomposed at 800°C. into potassium sulfate, alumina, sulfur trioxide, and water, while at 960°C. potassium aluminate is formed. A survey of the literature shows that it is commonly recommended to roast the alunite and then extract the potassium sulfate.

MacCarthy[6] heats alunite to 500°F. in the absence of air and then dumps it into water, thereby dissolving the soluble sulfates of potassium and aluminum. Cameron[7] roasts the ground alunite and then extracts the soluble alum. This is decomposed by heating and the evolved sulfur gases used to convert unchanged alumina into the sulfate. In a French patent[8] the alunite is crushed and then calcined until the aluminum sulfate is decomposed. The potassium sulfate is leached out and recovered by crystallization.

According to Chappell,[9] very little aluminate is formed when alunite is slowly heated to 750 to 1000°C. in a strong current of air. The

[1] CHAPPELL, H. F., U. S. Pat. 1,336,508, Apr. 13, 1920.

[2] DETWILLER, H. J., U. S. Pat. 1,274,145, July 30, 1918.

[3] PETIT-DEVAUCELLE, Fr. Pat. 524,810, Sept. 10, 1921.

[4] MEYERS, H. H., U. S. Pat. 1,314,280, Aug. 26, 1919.

[5] BOWLEY, H., *Proc. Roy. Soc. West Australia*, 7, 48 (1921).

[6] MACCARTHY, F. B., U. S. Pat. 1,413,045, Apr. 18, 1922.

[7] CAMERON, F. K., U. S. Pat. 1,233,977, July 17, 1917.

[8] SOCIÉTÉ DIOR FILS, Fr. Pat. 419,854, Jan. 17, 1911.

[9] CHAPPELL, H. F., U. S. Pat. 1,070,324, Aug. 12, 1913.

alumina becomes insoluble in water, while the potassium sulfate becomes soluble.   In later patents[1] he states that the calcination of alunite can best be carried out in two steps.   The alunite is first heated to 600°C. in the regular manner, since only a small amount of sulfur gases are given off at this temperature.   The material is then transferred to a closed retort and heated to 900 to 1000°C. while the sulfur gases are collected.   Some of the heat expended in calcining the alunite can be utilized for the extraction of the potassium sulfate by dumping the hot product into the liquid.[2]   He also describes a calcining apparatus[3] for alunite consisting of a rotary kiln so constructed that the products of combustion coming from the fuel are completely oxidized before mingling with the fumes of oxides of sulfur.   After passing through the cooler part of the kiln, the alunite is then further heated to complete the calcination, by direct heating in the combustion zone.[4]   It is claimed that more effective heating is obtained and very little potash is lost by volatilization, because the potassium sulfate partially fuses and forms a protective coating on the surface of the particles, which are then quickly removed from the high temperature zone.

Silsbee[5] roasts the alunite at 700 to 800°C. and then quenches the hot ore in a mother liquor of potassium sulfate.   The mixture is then passed through classifiers which remove the silica but leave the finely divided alumina in suspension.   After removing the alumina by means of thickeners, the solution is evaporated and the potassium sulfate crystallized.

According to Hagedorn,[6] the alunite is first calcined and then digested with hot water under a pressure of 50 to 70 pounds to dissolve the potassium sulfate and leave the alumina in a granular form easy to filter.

Spence and Llewellyn[7] calcine the alunite and recover the alumina by means of sulfurous acid.   Moldenke[8] mixes the alunite with sulfuric acid and then heats the mixture to form bricks which are broken up and heated to a higher temperature.   After leaching with water, the potash alum is crystallized and removed from solution, and then ammonium sulfate is added in order to crystallize ammonium alum.

[1] CHAPPELL, H. F., U. S. Pats. 1,089,109; 1,089,110, Mar. 3, 1911.   See also U. S. Pat. 1,195,655, Aug. 22, 1916.

[2] CHAPPELL, H. F., U. S. Pat. 1,268,433, June 4, 1918.

[3] CHAPPELL, H. F., U. S. Pat. 1,317,686, Oct. 7, 1919.

[4] CHAPPELL, H. F., U. S. Pats. 1,401,136; 1,401,137, Dec. 27, 1921.

[5] SILSBEE, J. L., U. S. Pat. 1,386,031, Aug. 2, 1921.

[6] HAGEDORN, C. F., U. S. Pat. 1,175,439, Mar. 14, 1916.

[7] SPENCE, H. and W. B. LLEWELLYN, U. S. Pat. 1,256,605, Feb. 19, 1918; Br. Pat. 109,998, Oct. 2, 1917.

See also YAMAZAKI, J. and J. FURUKAWA, *J. Soc. Chem. Ind.* (Japan), **29**, 147–53 (1926); *C. A.* **20**, 3,335 (1926).

[8] MOLDENKE, R., U. S. Pat. 1,637,451, Aug. 2, 1927.

In the process of Matheson,[1] it is claimed that the grinding and drying of the ore before roasting is unnecessary and that no extraneous supply of sulfuric acid is required.   The alunite is first roasted or calcined in the absence of air and the evolved gases used to treat a second portion of previously roasted alunite in the presence of sufficient water to produce strong sulfuric acid.   The temperature of the gases coming from the roasted alunite is between 400 and 500°C. and no other heat is necessary for the second reaction.   The iron oxide in the alunite acts as a catalytic agent for the combination of sulfur dioxide and oxygen.   The final product is leached with water and, after crystallizing the alum, the excess aluminum sulfate is also recovered by crystallization.

In the patent to Downs,[2] the alunite is first fused with an alkali to obtain the soluble sodium and potassium compounds.   The insoluble alumina is fused with sodium carbonate and the soluble alkali aluminate treated in the usual way.   Williams[3] fuses the alunite with alkali carbonate to form alkali aluminate.   The mass is leached with water and the alumina precipitated with special furnace gases resulting from incomplete combustion of soft coal.

According to MacDowell,[4] the sodium and potassium salts are volatilized when the alunite is heated at 1100 to 1600°C.   The addition of carbon lowers the temperature and, contrary to what might be expected, is said not to result in the formation of aluminate.   Hershman and Cooke[5] heat a mixture of alunite and carbon in a reducing atmosphere at a low temperature and obtain alumina and potassium aluminate.   The alumina is alkali-soluble and may be treated in the regular manner.   In a patent to Hershman,[6] the potassium aluminate is extracted with hot water under a pressure of 150 to 175 pounds.   It is also stated that all the alumina may be converted to aluminate by adding the necessary amount of potassium salt to the original charge.

Shoeld[7] mixes the alunite with a small amount of carbon and heats in a reducing atmosphere until the aluminum sulfate, but not the potassium sulfate is decomposed.[8]

In another patent to Hershman,[9] the alunite is heated with lime and alkali chloride in the presence of superheated steam to a temperature

[1] MATHESON, A., Br. Pat. 167,555, Aug. 8, 1921.

[2] DOWNS, W. F., U. S. Pat. 1,338,428, Apr. 27, 1920.

[3] WILLIAMS, G. L., U. S. Pat. 1,559,189, Oct. 27, 1925.

[4] MACDOWELL, C. H., U. S. Pat. 1,136,519, Apr. 20, 1915; Br. Pat. 5563 (1915), Sept. 30, 1915.

[5] HERSHMAN, P. R., and R. D. COOKE, U. S. Pat. 1,189,254, July 4, 1916.   See also PETIT-DEVAUCELLE, L., Fr. Pat. 524,810, Sept. 10, 1921.

[6] HERSHMAN, P. R., U. S. Pat. 1,191,105, July 11, 1916.

[7] SHOELD, M., U. S. Pat. 1,401,741, Dec. 27, 1921.

[8] See JANES, F. W., *Bull. Commonwealth Australia, Advisory Council Sci. Ind.*, 1917, No. 3, 38 pp.; *C. A.* **13**, 299 (1919).

[9] HERSHMAN, P. R., U. S. Pat. 1,191,104, July 11, 1916.

not exceeding 1400°C. Soluble alkali aluminate is obtained by digesting with hot water, preferably under presssure. The alumina contained in the residue may be extracted with alkali. By using 30 parts of lime to 100 parts of alunite and heating to 1000°C. in the presence of steam, 40 per cent of the total alumina is said to be obtained as soluble $2Al_2O_3.K_2O$.[1]

Mitchell[2] adds enough limestone to the alunite to combine with the sulfates as well as the silicates. By heating at 1100 to 1300°C., a granular or porous alkaline earth aluminate is obtained, which is easily leached with sodium carbonate. Downs[3] seems to think that a preliminary heating of the alunite with a basic substance offers the best method for the treatment of the ore.

Fox[4] heats a mixture of alunite and fluorspar (3 equivalents of fluorspar to 1 equivalent alumina) to red heat and obtains soluble potassium sulfate and insoluble calcium sulfate and aluminum fluoride.

Blough and McIntosh[5] sinter a mixture of finely ground alunite and sodium chloride at a temperature of 800°C. The soluble sodium and potassium sulfates are separated and the sodium sulfate heated with the insoluble alumina to a temperature less than 1500°C. to form soluble sodium aluminate.

Cross[6] heats a mixture of alunite and sodium chloride at 500 to 700°C. in the presence of superheated steam. The sodium and potassium sulfates are soluble and are removed by leaching. The insoluble alumina is then heated with carbon and sodium sulfate to 1250°C. to form soluble aluminate. The operation may be carried out with a single fusion.

HYDROCHLORIC ACID PROCESSES

Compared with sulfuric acid, hydrochloric acid has the fundamental disadvantage of a considerably higher cost. In general, it must be made by the reaction of sulfuric acid on salt or a similar material, and the market price of the sulfate obtained is so low that a good share of the labor, material, and expense costs of the process must be charged against the acid itself. Moreover, its greater chemical activity and the greater solubility of its salts complicates the apparatus problem for any industry using it, since there is no available commercial metal of reasonable

[1] HERSHMAN, P. R., U. S. Pat. 1,240,570, Sept. 18, 1917.

[2] MITCHELL, T. A., U. S. Pat. 1,628,174, May 10, 1927.

[3] DOWNS, W. F., *Eng. Mining J.*, **107**, 388 (1919).

[4] Fox, J. F., U. S. Pat. 1,217,432, Feb. 27, 1917.

[5] BLOUGH, E. and T. McINTOSH, U. S. Pat. 1,214,991, Feb. 6. 1917.

[6] CROSS, R., U. S. Pat. 1,301,394, Apr. 22, 1919.

price which has an adequate resistance to solution by this acid. Acid-proof brick, stoneware, rubber, and for the very dilute solutions, wood, are materials of construction which introduce both expense and difficulty into a chemical process. The gaseous nature of the acid and the fuming of its strong solutions complicate the corrosion problem.

On the other hand, the peculiar solubility relations of the chlorides in the presence of an excess of the acid, and the fact that when its salts are decomposed by heat the acid itself is not decomposed and may be readily and quite completely recovered from even dilute gaseous mixtures, give it certain compensating advantages over sulfuric acid.

Bauxite, clay, etc., are generally very readily attacked by hydrochloric acid, although it has been recommended[1] to calcine them first, particularly[2] in an oxidizing atmosphere or in the presence of an oxidizing agent. A preliminary heating with a small amount of sodium carbonate[3] and a preliminary treatment with sulfuric acid[4] also have been recommended. Less silica is said to be dissolved[5] if the acid concentration in the solution is kept moderately low, fresh acid being added as the mineral is dissolved.

The relative insolubility of aluminum chloride in a concentrated hydrochloric acid solution permits a fairly complete separation of aluminum from iron and some other impurities. By passing the gas into the impure solution,[6] the hydrated crystalline aluminum chloride is readily precipitated. The iron should be in the ferric condition.[7]

Blanc makes use of the fact that if large amounts of alkali chlorides are present, as will be the case in solutions of leucite or similar potash-bearing rocks, the greater part of the alkali chloride may be removed in a substantially pure state by frac-

[1] LADD, E., Br. Pat. 18,925 (1909), Nov. 18, 1909.

[2] BRUNEL, J. M. A., Fr. Pat. 587,199, Apr. 11, 1925.

[3] LE VERRIER and MINET, Fr. Pat. 244,582, Jan. 24, 1895.

[4] GOOCH, F. A., U. S. Pats. 558,725; 558,726, Apr. 21, 1896.

[5] GIORDANI, F., U. S. Pat. 1,196,264, June 3, 1921; Fr. Pat. 540,713, July 17, 1922; Ger. Pat. 426,832, Mar. 20, 1926.

[6] GLADYSZ, T., Ger. Pat. 21,154, Feb. 3, 1883.

GOOCH, F. A., U. S. Pats. 558,725; 558,726, Apr. 21, 1896

SALZWERK HEILBRON, K. SCHMIDT, K. FLOR, Ger. Pat. 455,172, Feb. 3, 1928.

[7] BRUNEL, J. M. A., Fr. Pat. 587,199, Apr. 11, 1925.

tional crystallization[1] before the aluminum chloride is precipi-
tated. If this precipitation with hydrochloric acid takes place
at 70°C., the rest of the alkali chloride remains in solution.
The Blanc process, outlined in Fig. 42, has been applied semi-
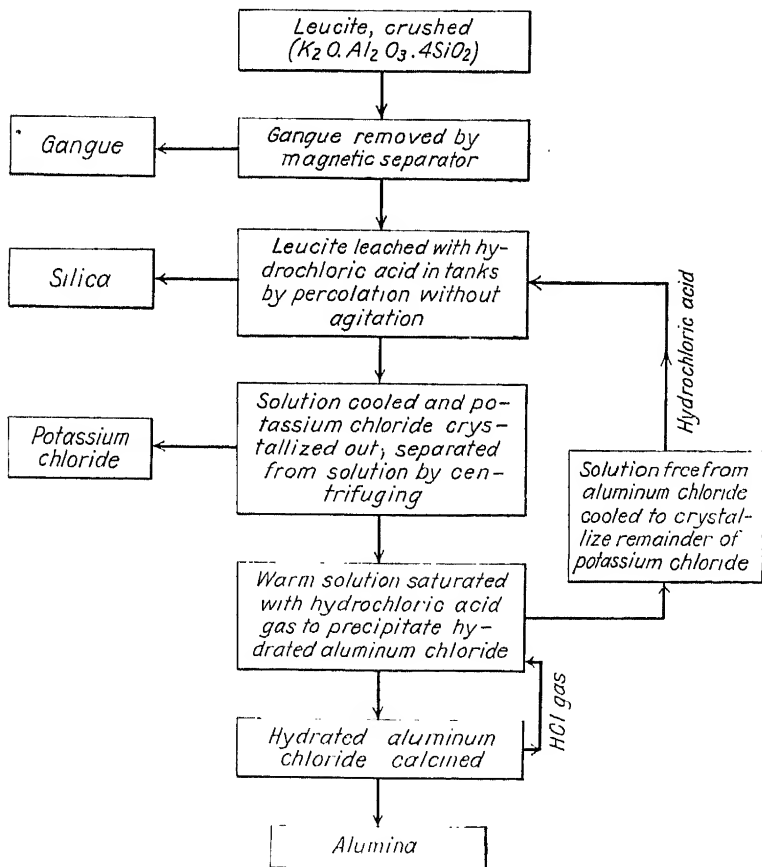
Fig. 42.   Diagram of Blanc leucite process for producing alumina.

commercially to the recovery of potassium chloride and alumina
from the extensive leucite deposits in the neighborhood of Rome
and Naples. The gangue in this ore is magnetic and can be
removed by a magnetic separator. Baron Blanc has found that

[1] BLANC, G. A., U. S. Pat. 1,656,769, Jan. 17, 1928; Br. Pat. 176,770,
Sept. 7, 1922; Fr. Pat. 547,923, Dec. 28, 1922; Ger. Pats. 361,959, Oct. 20,
1922; 379,511, Aug. 24, 1923; Norw. Pat. 38,055, Oct. 15, 1923.

if the leaching with hydrochloric acid is carried out by percolation without disturbing the porous mass, the silica will remain in place when the solution is drawn off (see p. 185). The commercial possibilities of the process depend upon the recovery of potassium chloride as well as alumina. Nitric acid may be employed instead of hydrochloric acid for leaching the leucite. Several rather complete descriptions of the leucite process[1] have been given in the various technical journals and the reader is referred to them for further information. Parravano[2] has discussed the recovery of alumina and potash from leucite from the physicochemical point of view. He has given, in this article, a very interesting series of data on the solubility relations in solutions of hydrochloric acid, aluminum chloride, and potassium chloride. Malquori[3] has investigated the systems involving the products obtained by treating leucite with hydrochloric or nitric acids.

The hydrochloric acid required for extraction may be obtained by calcination of the previously prepared aluminum chloride,[4] and the precipitated salt may be washed in a concentrated solution of aluminum chloride or hydrochloric acid. The last traces of hydrochloric acid may be removed from the crystals by washing with a basic aluminum chloride solution,[5] which can be made by dissolving alumina in aluminum chloride.[6]

To avoid the difficulties involved in handling and absorbing such a large amount of hydrochloric acid gas, various inventors recommend

[1] BLANC, G. A., *Atti II congresso naz. chim. pura applicata*, pp. 1398-1405; *Atti congresso naz. chim. ind.* (1924), 119 130; *Giorn. chim. ind. applicata* **7**, 3–12 (1924); FRYDLENDER, J. H., *Rev. prod. Chim.* **28**, 217 222 (1925); HINCHLEY, J. W., *Chem. Ind.* **43**, 158 168 (1924); POMILIO, U., *Chim. ind.* **7**, 425–437 (1922); THORSSELL, T., *Z. angew. Chem.* **39**, 1593 1597 (1926).

[2] PARRAVANO, N., *Giorn. chim. ind. applicata* **10**, 501 (1928).

[3] MALQUORI, G., *Gazz. chim. ital.* **57**, 661-666 (1927).

[4] HÖGANÄS BILLESHOLMS AKTIEBOLAG, U. S. Pat. 1,403,061, Jan. 10, 1922; Br. Pats. 153,500, Nov. 11, 1920; 159,086, Feb. 24, 1921; 217,568, May 14, 1925; Fr. Pats. 508,799; 508,800, Oct. 22, 1920; 585,769, Mar. 6, 1925; Dan. Pat. 27,058, Dec. 27, 1920; Ger. Pat. 339,788, Aug. 11, 1921; Norw. Pat. 32,547, June 27, 1921; Swed. Pats. 51,520, Apr. 26, 1922; 59,865, Nov. 17, 1925; 62,581, Mar. 15, 1927; Swiss Pats. 86,845, Oct. 1, 1926; 86,846, Oct. 16, 1920; SIEURIN, S. E., U. S. Pat. 1,701,510, Feb. 12, 1929.

[5] HOWARD, H., U. S. Pat. 1,430,449, Sept. 26, 1922.

[6] LOEWIG, F., Br. Pat. 1,444 (1879), applied for Apr. 10, 1879. Void.

simple crystallization of the aluminum chloride from the solution.[1] The resulting crystals may be washed with hydrochloric acid,[2] preferably saturated with aluminum chloride,[3] in order to remove impurities. Iron may be removed (probably only in part) from this solution by treatment with pure alumina.[4] The same reaction is recommended[5] for purifying the original hydrochloric acid solution, by using an excess of the aluminous mineral during the solution process. Elsewhere[6] the addition of alumina is used to precipitate a basic aluminum chloride. It has also been proposed[7] to remove iron from the neutralized chloride solution by electrolysis.

In an early English patent,[8] the iron is reduced to the ferrous state and the alumina is precipitated out of this solution by the addition of alkaline earth carbonate. After reducing the iron, the solution may be evaporated and the dried salts heated to 300°C. in a reducing atmosphere containing moisture.[9] It is stated that the aluminum chloride is decomposed and rendered insoluble, while the ferrous chloride remains in a soluble form. If the iron is not reduced, it is stated[10] that on heating the mixed chlorides, the ferric chloride is decomposed, while the aluminum chloride remains in a water-soluble form. Giraud[11] heats the mixed chlorides of aluminum and iron so as to volatilize them and passes the vapor over iron filings. The ferric chloride is reduced to ferrous chloride, which is less volatile than the aluminum chloride, and therefore remains behind. Obviously this reaction could only be applied to a mixture of the anhydrous chlorides, since the hydrated chlorides

[1] GIORDANI, F., U. S. Pat. 1,496,264, June 3, 1924; Fr. Pat. 540,713, July 17, 1922; Ger. Pat. 426,832, Mar. 20, 1926.

[2] SPECKETER, H., and F. ROSSTEUTSCHER, Ger. Pat. 442,967, Apr. 11, 1927.

[3] SPECKETER, H., G. MÜNCH, and F. ROSSTEUTSCHER, U. S. Pat. 1,519,880, Dec. 16, 1924; Br. Pat. 205,563, Oct. 18, 1923; Fr. Pat. 569,176, Apr. 12, 1924; Ger. Pat. 414,128, June 25, 1925; Norw. Pat. 40,380, Dec. 1, 1924; Swed. Pat. 57,129, Sept. 11, 1924; Swiss Pat. 101,397, Nov. 1, 1923.

[4] CHEM. FAB. GRIES.-ELEK., Br. Pat. 240,834, May 13, 1926; Norw. Pat. 43,144, Oct. 11, 1926.

[5] PEDEMONTE, A., U. S. Pat. 1,490,021, Apr. 8, 1924; Fr. Pat. 547,862 Dec. 27, 1922; Add. Pat. 26,367, Nov. 13, 1923; Swiss Pat. 101,612, Oct. 1, 1923.

[6] LAUR, Fr. Pat. 220,790, Apr. 8, 1892.

[7] POMILIO, U. and F. GIORDANI, U. S. Pats. 1,556,543, Oct. 6, 1925; 1,559,179, Oct. 27, 1925.

[8] RICHARDSON, H., Br. Pat. 8,382 (1885), applied for July 11, 1885.

[9] CHEM. FAB. GRIES.-ELEK., Br. Pat. 211,184, May 13, 1926; Ger. Pat. 357,900, Sept. 4, 1922. SPECKETER, H., U. S. Pat. 1,672,788, June 5, 1928. I. G. FARBENINDUSTRIE, A.-G., Norw. Pat. 44,059, May 30, 1927.

[10] NOBLE, A., Br. Pat. 2,136 (1862), applied for July 28, 1862. See also HART, E., U. S. Pat. 1,323,228, Nov. 25, 1920.

[11] GIRAUD, L., Fr. Pat. 584,244, Feb. 2, 1925.

hydrolyze and decompose instead of volatilizing on heating. It has been proposed[1] to separate the resulting oxides by differences in specific gravity or other means. Lime may be removed[2] before evaporating as sulphate or sulphite.

If the double chloride of sodium and aluminum be heated in steam[3] to a sufficient temperature, the acid is given off and soluble sodium aluminate formed. It has been proposed[4] to perform the evaporation in a special furnace whose lining may be transferred to the calciner with the dried salt.

After the pure aluminum chloride has been obtained, it may be converted into alumina by any of the precipitation methods discussed in connection with the sulfuric acid processes. In general, however, it appears to be preferable to decompose the hydrated salt by calcination and thus recover the acid for re-use in the process.[5] By calcining at a lower temperature and removing the remaining chlorine by means of an alkaline substance, alumina more readily soluble in an acid is obtained.[6] Hydrochloric acid vapors also can be used for the manufacture of chlorine.[7]

Pure aluminum sulfate may be produced and the hydrochloric acid recovered by treating the aluminum chloride crystals with concentrated sulfuric acid.[8] It is alleged that the chloride may be converted into fluoride by heating at 300 to 400°C. with hydrofluoric acid.[9] The conversion of the sulfate into the chloride by metathesis with salt and crystallizing out the sodium sulfate has also been recommended.[10]

HYDROFLUORIC ACID PROCESSES

The fact that hydrofluoric acid and certain fluorides attack silica has led numerous inventors to propose their use in extracting alumina from its ores, particularly silicates. It is to be noted, however, that aside from the expensive nature of the acid and its seriously injurious physiological effects, the fact that it attacks the silica makes it lose one of the chief advantages of the acid processes. Since, however, the aluminum industry uses large quantities of materials containing aluminum fluoride

[1] LADD, E., Br. Pat. 18,925 (1909) Nov. 18, 1909.

[2] ELLIOTT, A. T., U. S. Pat. 1,327,536, Jan. 6, 1920.

[3] YNGSTRÖM, L., and A. R. LINDBLAD, Swed. Pat. 41,110, Aug. 9, 1916.

[4] WELFORD, R., Br. Pat. 118,312, Aug. 19, 1918.

[5] SPECKETER, H. and E. C. MARBURG, Ger. Pat. 438,745, Dec. 24, 1926; addition to 414,128.

[6] MARBURG, E. C., F. ROSSTEUTSCHER, Ger. Pat. 452,457, Nov. 11, 1927.

[7] WELFORD, R., Br. Pat. 130,164, July 28, 1919.

[8] CHEM. FAB. GRIES.-ELEK., Ger. Pat. 424,129, Jan. 18, 1926.

[9] LE VERRIER and MINET, Fr. Pat. 244,582, Jan. 24, 1895

[10] LINDBLAD, A. R. and G. H. HULTMAN, Swed. Pat. 53,664, Feb 7, 1923

(cryolite, chiolite, aluminum fluoride, etc., see Chap. VIII), these processes have a certain interest as offering possibilities for the economical manufacture of such materials, although there is probably no chance that they could be economically used for the manufacture of alumina itself.

One of the most serious difficulties in connection with such processes is the peculiarity of aluminum fluoride, by virtue of which it may be deposited out of aqueous solutions as an insoluble crystalline hydrate, probably $Al_2F_6.7H_2O$. This deposition takes place whenever the solution is heated, the rate being dependent on temperature, acidity, and perhaps other factors. Obviously, in most processes of attacking aluminum ores with hydrofluoric acid or fluorides, there will be more or less of this salt precipitated and, therefore, more or less loss of both fluorine and alumina in the mud of the undissolved silica, etc., which is filtered off. In fact, this fluorine loss is one of the principal reasons for the lack of practical success of some of these processes. The addition of small amounts of hydrofluoric acid in connection with other acid processes has been or will be discussed in connection with such processes, so that this section will deal only with processes of attacking ores by either hydrofluoric acid or soluble fluorides.

Clay or kaolin, preferably calcined at a low temperature, reacts readily with hydrofluoric acid or hydrofluosilicic acid to form substantially neutral aluminum fluoride solutions.[1] If an excess of clay is used, the silica is largely left in an insoluble and somewhat granular form. It also has been recommended[2] to treat the moist clay with hydrofluoric acid or silicon tetrafluoride, to form first an acid solution and, ultimately, a neutral solution of aluminum fluoride, the excess of clay precipitating out iron and silica. An alternative procedure of the same inventor consisted in calcining kaolin with a considerable amount of aluminum fluoride so as to volatilize the silica. Bauxite

[1] ACKERMANN, W., U. S. Pat. 508,796, Nov. 14, 1893; Br. Pat. 15,083 (1892) June 24, 1893; Ger. Pat. 69,791, June 20, 1893; Norw. Pat. 2,953, applied for Aug. 20, 1892; Swed. Pat. 4,481, Sept. 2, 1893.

RÜTGERSWERKE, A.-G., and J. DOMANSKY, Br. Pat. 234,485 (Void), applied for May 19, 1925; Fr. Pat. 597, 760, Nov. 28, 1925; Norw. Pat. 44,057, May 30, 1927.

[2] CHILDS, D. H., U. S. Pats. 1,036,453; 1,036,454, Aug. 20, 1912. See also *Met. Chem. Eng.*, **11**, 231 (1913); YAMAZAKI, Z., M. YASUDA, T. TAKAMATSU, Jap. Pat. 41,807, Feb. 18, 1922; (*C. A.* **18**, 448 (1924)).

may also be dissolved by hydrofluoric acid[1] and the solution treated in a similar way.

Doremus has done a good deal of experimental and semi-commercial scale work on fluoride processes for extracting alumina from clay, feldspar, etc.[2,3]   After a preliminary roast at about 540°C., the ore was attacked with 10 per cent hydrofluoric acid and potash, if present, was separated as the insoluble fluosilicate.   An excess of clay was used to precipitate silica from the aluminum fluoride solution and, after filtration, the aluminum fluoride was precipitated by heating the neutral solution under pressure in a digester.[4]   The aluminum fluoride was to be decomposed by sulfuric acid in order to recover the fluorine, but unfortunately experiment shows that it is very difficult to carry out this reaction.   It was later proposed to decompose the fluoride by feeding it into a flame of burning oil or gas, collect the alumina powder by settling, and scrub out the hydrofluoric acid gas from the products of combustion.   Installation expenses and fluorine losses would undoubtedly make this impractical.

Hydrofluosilic acid was originally recommended by Le Chatelier,[5] who made it by passing steam over a highly heated mixture of fluorspar and silica and used it to attack clay to form soluble aluminum fluosilicate.   By double decomposition with sodium chloride solution, there were produced insoluble sodium fluosilicate and an aluminum chloride solution, which was treated with excess of caustic soda to form sodium aluminate.   Alumina was recovered from this in the usual way. Gibbs[6] likewise attacked clay with hydrofluoric acid but proposed to recover the fluorine by treating the resulting fluosilicates with sulfuric acid.   Kern[7] formed aluminum fluosilicate from clay and hydrofluoric acid.

It has also been proposed[8] to attack feldspar with solutions of the fluosilicates of aluminum, sodium or ammonium, so as to produce potassium fluosilicate which may be extracted from the residue with hot water.

Betts[9] boils kaolin, etc., with a solution of ammonium fluoride, ammonia being given off and collected.   It was alleged that aluminum

[1] Gin, G., Aust. Pat. 16,365, May 25, 1904.

[2] Doremus, C. A., U. S. Pats. 1,054,518, Feb. 25, 1913; 1,237,488, Aug. 21, 1917; 1,391,172, Sept. 20, 1921; Fr. Pat. 506,392, Aug. 20, 1920.

[3] See also McLhiney, P. C., U. S. Pat. 1,083,691, Jan. 6, 1914.

[4] Doremus, C. A., U. S. Pat. 1,110,675, Sept. 15, 1914.

[5] Le Chatelier, Br. Pat. 413 (1858), applied for Mar. 2, 1858.

[6] Gibbs, W. T., U. S. Pat. 772,657, Oct. 18, 1904; Ger. Pat. 173,902, July 26, 1906.

[7] Kern, E. F., U. S. Pat. 963,156, July 5, 1910.

[8] Blackmore, H. S., U. S. Pat. 1,355,381, Oct. 12, 1920.

[9] Betts, A. G., U. S. Pat. 1,300,110, Apr. 8, 1919.

fluoride would form and go into solution, from which alumina could be precipitated by adding ammonia after cooling. Unfortunately, laboratory tests show that, as would be expected, it is silica rather than alumina which goes into solution in this reaction. This solubility of silica in ammonium fluoride is used by McClenahan[1] to extract silica from silicates, leaving potassium fluosilicate and the insoluble aluminum hydrate to be treated chemically by other reagents. The excess of silica is precipitated from the ammonium fluosilicate solution by the ammonia which was given off during the boiling process. On heating the insoluble residues to 300 to 400°C. in the presence of steam, the aluminum ammonium fluorides are decomposed and ammonium fluoride recovered. Potassium fluosilicate may remain with the alumina and its fluorine be recovered by treatment with sulfuric acid, or it may be vaporized with the ammonium salts.

In recent foreign patents granted to Seglem-Svendsen[2] the dried aluminous material, such as feldspar, is heated with an ammonium fluoride solution at 34 to 100°C. Ammonia escapes and the bifluoride of ammonium decomposes the clay. This mixture is evaporated and heated to about 300°C. to drive off the volatile fluorides of silicon, ammonium, titanium, and vanadium. The remaining fluorides are heated at 400 to 500°C. in the presence of a reducing gas to reduce iron and remove the last of the volatile fluorides. The material is then heated with a mixture of dry hydrochloric acid and ammonia gas (free from oxygen and carbon dioxide). The volatile chlorides of ammonium and aluminum are separated by fractional condensation and the aluminum chloride heated with moisture to form alumina and hydrochloric acid. Silica gel and potassium chloride are by-products of a very complicated process and in order to pay for the evaporation of solutions and dry distillations, the by-products would have to command a fancy price.

Doremus' process of recovering aluminum fluoride from solutions by converting it into an insoluble form by digestion under pressure at elevated temperatures has already been mentioned. Milligan[3] finds that a granular aluminum fluoride which is easy to filter can be precipitated at temperatures below the boiling point if the solution is properly acidified with hydrofluoric acid. Ackermann[4] had previously proposed to crystallize aluminum fluoride (apparently one of the

[1] McCLENAHAN, F. M., U. S. Pats. 1,426,890; 1,426,891, Aug. 22, 1922.

[2] SEGLEM-SVENDSEN, S., Br. Pat. 279,515, Sept. 27, 1928; Norw. Pat. 45,918, Dec. 31, 1928; Fr. Pat. 643,981, Sept. 29, 1928.

[3] MILLIGAN, L. H., U. S. Pat. 1,403,183, Jan. 10, 1922.

[4] ACKERMANN, W., U. S. Pat. 513,971, Feb. 6, 1894; Danish Pat. 26, Apr. 22, 1895; Ger. Pat. 70,155, July 3, 1893; Norw. Pat. 2,954, applied for Dec. 10, 1892; Swed. Pat. 4,488, Sept. 2, 1893.

soluble forms) from solution after reducing the iron to the ferrous state. Mellen[1] proposes to precipitate aluminum fluoride from a sodium and aluminum sulfate solution by means of sodium fluoride. The whole question of the different hydrates of aluminum fluoride, their relationship to one another, and their solubility has been studied by Tosterud.[2]

The aluminum fluoride obtained may be decomposed by superheated steam[3] in retorts. It also has been proposed to add this to the fused fluoride bath (used in producing aluminum) in the presence of steam and recover the hydrofluoric acid.[4] This is, of course, quite impractical. The addition of lime and caustic soda to precipitate insoluble fluoride, and the conversion of the alumina to sodium aluminate also have been proposed.[5] Of course, the solution may be converted into artificial cryolite by the addition of alkali fluorides,[6] after which treatment with water and lime[7] will give a pure calcium fluoride and a soluble alkali aluminate, as in early processes of manufacturing soda and alumina from natural cryolite.

NITRIC ACID PROCESSES

The recent developments in the field of fixation of atmospheric nitrogen, by which synthetic nitric acid is cheaply produced and converted into nitrates for use as fertilizers, have caused many inventors to work on nitric acid processes for extracting alumina from certain ores. In general, only such ores would be attractive as contain other base metals which, in the process of producing the alumina, could be recovered as nitrates suitable for fertilizer purposes. Such minerals are primarily those containing potash as well as alumina, such as potash feldspar (orthoclase) and leucite. A good deal of work also has been done in Norway[8] on the feldspars high in lime, such as labradorite, because of their abundance and the fact that much basic calcium nitrate has been commercially produced in Norway and sold as a fertilizer.

[1] Mellen, G., U. S. Pat. 1,160,131, Nov. 16, 1915.

[2] Tosterud, M., *J. Am. Chem. Soc.*, **48**, 1 5 (1926).

[3] Doremus, C. A., U. S. Pat. 725,683, Apr. 21, 1903; Br. Pat. 9,021 (1903), Aug. 27, 1903; Fr. Pat. 331,400, Sept. 10, 1903.

[4] McIlhiney, P. C., U. S. Pat. 1,083,691, Jan. 6, 1914.

[5] Doremus, C. A., U. S. Pat. 1,215,351, Feb. 13, 1917.

[6] Betts, A. G., U. S. Pat. 1,524,472, Jan. 27, 1925.

[7] Rivière, L., Fr. Pat. 396,148, Apr. 9, 1909; 1st Add. 10,161, May 12 1909; 2nd Add. 10,451, July 12, 1909; 3rd Add. 10,809, Oct 8, 1909.

[8] Goldschmidt, V. M., *Tids. Kemi*, **16**, 21 24 (1919).

Like hydrochloric and hydrofluoric acids, nitric acid is generally more expensive than sulfuric acid; but unlike them, its salts on thermal decomposition do not regenerate the free acid unchanged, as the acid is largely decomposed into oxides of nitrogen, which require reoxidation to form nitric acid. The problem of recovering the acid from the aluminum nitrate, therefore, resembles to a certain extent the problem of recovering sulfuric acid from aluminum sulfate, although aluminum nitrate is decomposed at a relatively low temperature, and this simplifies the matter considerably.

It is somewhat easier to obtain suitable materials of construction for nitric acid than for hydrochloric acid processes, since certain iron alloys resist nitric acid very well, and metallic aluminum itself is also very resistant if the acid is free from the halogens. However, the tendency of the acid to react with all wood or similar organic material to produce oxidized and dangerously inflammable compounds would complicate the operation of such a process to a certain extent.

In general, the pulverized mineral is attacked by simply heating it with diluted nitric acid. According to Halvorsen,[1] however, the decomposition of the clay may be facilitated by digesting the mixture of clay and acid for 10 hours with 40 per cent nitric acid under a pressure of 4 atmospheres. If leucite is treated with a limited quantity of nitric acid, it is alleged that the potassium oxide goes into solution first, leaving the alumina undissolved.[2] A second treatment with nitric acid dissolves this alumina. It also has been proposed[3] to decompose labradorite and similar rocks by heating them at 300 to 600°C. with the oxides of nitrogen, in the presence of water vapor. Soluble alkali nitrates are formed and the alumina is left in a form in which it may be readily dissolved by acids. Mention also should be made of an impractical proposal[4] to heat red bauxite with air in the presence of alkali or alkaline earth carbonates and an oxidizable substance, such as ferrous sulfide, to form nitrates. Twynam[5] treats aluminous slag with nitric acid and, after filtering, adds lime to precipitate calcium aluminate, which in turn is treated with soda to obtain sodium aluminate.

[1] HALVORSEN, B. F., Br. Pat. 120,035, Mar. 6, 1919; Swed. Pat. 48,606, Feb. 23, 1921.

[2] NORSK HYDRO-ELEK. KVAEL., Fr. Pat. 529,570, Dec. 1, 1921.

[3] GOLDSCHMIDT, V. M. and O. RAVNER, U. S. Pat. 1,302,852, May 6, 1919; Br. Pat. 113,278, Jan. 23, 1919; Ger. Pat. 339,819, Aug. 12, 1921; Norw. Pat. 30,823, June 21, 1920; Swed. Pat. 46,925, May 5, 1920.

[4] LEGESNE, N., Fr. Pat. 437,397, Apr. 19, 1912.

[5] TWYNAM, T., Br. Pat. 20,258 (1914) Sept. 9, 1915.

As in the other acid processes, the elimination of iron has been attempted in a variety of ways. It is claimed[1] that if bauxite or clay be first heated to about 500°C. in a reducing atmosphere, the solubility of the alumina in nitric acid is increased, while the iron (reduced to Fe_3O_4) becomes practically insoluble. In the case of labradorite, the same inventors[2] first treat the mineral with the acid in a countercurrent scheme which gives them a neutral solution low in iron and silica, and then remove the remaining iron from the solution by adding alumina or potassium ferrocyanide or both, and holding the solution at 40°C. for some time. The iron precipitate carries down any colloidal silica which may be present. A pressure digest with an excess of alumina is said to precipitate the iron.[3]

Mejdell[4] removes iron from an aluminum nitrate solution by first treating it with enough calcium carbonate to change at least 2 per cent of the contained alumina into a soluble basic compound. Ferric oxide, made by decomposing ferric nitrate at 400°C., is added as a catalyst and the solution is held at 80°C. for some time. Under proper conditions, all of the iron precipitates in a form that is easy to filter, but if too much of the acid has been neutralized, the iron precipitates too rapidly and is difficult to filter. The catalytic properties of the ferric oxide are injured if it is heated to a temperature as high as 600°C. After the iron has been removed, alumina, ammonia, or more limestone may be added to precipitate the alumina.[5]

Separation by crystallization has also been proposed. Mejdell and Ravner[6] make the solution basic by adding alumina or lime until the iron nearly precipitates. By pouring a warm saturated solution into a cold saturated solution, small aluminum nitrate crystals are precipi-

[1] GOLDSCHMIDT, V. M. and O. RAVNER, U. S. Pat. 1,357,089, Oct. 26, 1920; Br. Pat. 122,623, Sept. 11, 1919; Fr. Pat. 493,804, Aug. 22, 1919; Ger. Pat. 339,211, July 16, 1921; Norw. Pat. 30,997, Aug. 16, 1920; Swed. Pat. 49,600, July 13, 1921.

[2] GOLDSCHMIDT, V. M. and O. RAVNER, U. S. Pat. 1,413,720, Apr. 25, 1922; Br. Pat. 125,578, Dec. 18, 1919; Fr. Pat. 520,988, July 5, 1921; Norw. Pat. 31,117, Sept. 27, 1920; Swed. Pat. 48,661, Mar. 2, 1921.

[3] CONWAY VON GIRSEWALD, F., and R. KAISER, Ger. Pat. 451,117, Oct. 21, 1927; BUCHNER, M., Br. Pat. 282,772, Dec. 24, 1926.

[4] MEJDELL, T., U. S. Pat. 1,421,804, July 4, 1922; Br. Pat. 139,470, Mar. 10, 1921; Fr. Pat. 510,426, Dec. 4, 1920; Ger. Pat. 355,850, July 8, 1922; Norw. Pats. 31,797, Feb. 21, 1921; 32,491, June 20, 1921; Swed. Pat. 51,459, Apr. 19, 1922.

[5] NORSK HYDRO-ELEK. KVAELS., Norw. Pat. 45,196, May 29, 1928.

[6] MEJDELL, T. and O. RAVNER, U. S. Pat. 1,575,634, Mar. 9, 1926; Fr. Pat. 548,035, Dec. 30, 1922; Norw. Pat. 36,430, Jan. 2, 1923; Swed. Pat. 55,767, Dec. 28, 1923.

tated which are free from iron. An alternative process[1] used with leucite and similar materials, involves crystallizing potassium and aluminum nitrates from a basic solution and recrystallization in the same type of solution.

Having removed as much as possible of the iron, we are faced with the problem of satisfactorily separating alumina from the nitrates of potassium, sodium, calcium, etc., which also may be present. Appar-
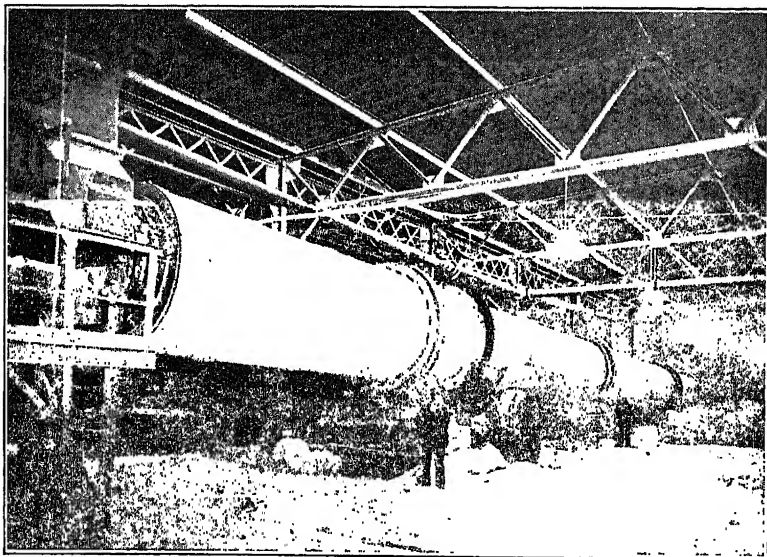
FIG. 43.— Kiln for calcining alumina.

ently, a basic aluminum nitrate may be precipitated by hydrolysis[2] on boiling for a long time a solution containing the nitrates of aluminum, sodium and calcium, fresh dilute solution being constantly added to keep the temperature at about 140°C. until 60 to 70 per cent of the acid has distilled off. About 80 per cent of the alumina precipitates as basic nitrate before the precipitation of iron begins. The basic nitrate may be decomposed with ammonia.[3]

[1] HALVORSEN, B. F., H. J. FALCK, T. MEJDELL, and O. RAVNER, U. S. Pat. 1,531,336, Mar. 31, 1925; Fr. Pat. 579,815, Oct. 24, 1924; Norw. Pat. 41,139, Mar. 30, 1925.

[2] MEJDELL, T., U. S. Pat. 1,413,754, Apr. 25, 1922; Br. Pat. 154,259, Nov. 10, 1921; Fr. Pat. 521,029, July 5, 1921; Ger. Pat. 346,763, Jan. 6, 1922; Norw. Pat. 31,700, Feb. 7, 1921; Swed. Pat. 50,302, Nov. 9, 1921; Swiss Pat. 91,153, Oct. 17, 1921.

[3] FOSS, A. and T. MEJDELL, U. S. Pat. 1,464,984, Aug. 14, 1923; Fr. Pat. 548,033, Dec. 30, 1922; Norw. Pat. 39,192, June 30, 1924.

A solution containing nitrates of potassium and aluminum may be partially separated by fractional crystallization,[1] nearly pure potassium nitrate crystallizing out at first.   The mixture of potassium and aluminum nitrates, which is later produced, may be separated by treatment with strong nitric acid, in which potassium nitrate is soluble but aluminum nitrate substantially insoluble.   The acid used for this purpose is then diluted and employed in digesting a fresh solution of leucite. The insolubility of aluminum nitrate in 60 per cent nitric acid also has been used to precipitate aluminum nitrate from a concentrated solution obtained by treating leucite with nitric acid.[2]   Milligan[3] has determined the solubility of aluminum nitrate in various strengths of nitric acid.

Aluminum nitrate may be converted into alumina and oxides of nitrogen by heating.[4]   If a mixture of aluminum nitrate and nitrates of the alkali or alkaline earth metals is heated, the aluminum nitrate is decomposed first, at about 300°C.,[5,6] leaving the alumina in a form which is easy to filter; after which the mass is extracted with water and filtered to remove unchanged alkali and alkaline earth nitrates.   Ferric nitrate may be decomposed by a preliminary heating at about 150°C., but aluminum nitrate starts to decompose at 140°C., so that the iron oxide will contain some alumina.   The necessity of dissolving the mass in water, filtering, and reëvaporating would make this method of removing iron rather expensive.   If the mixture is heated to 300°C., both iron oxide and alumina are formed and may be separated by "the action of an acid which dissolves the combined iron but does not affect the aluminum oxide."

Later patents[7] recommend that the mixed salts be heated to 400°C. in order to insure complete decomposition of the aluminum nitrate.

[1] Falck, H. J., U. S. Pat. 1,667,968, May 1, 1928; Br. Pat. 230,015, July 23, 1925; Fr. Pat. 593,619, Aug. 28, 1925; Norw. Pat. 41,581, July 6, 1925. Craig, T. J. I. and Peter Spence and Sons, Ltd., Br. Pat. 283,087, Dec. 29, 1927.

[2] Società Italiana Potassa, Br. Pat. 246,827, Dec. 9, 1926; Fr. Pat. 602,276, Mar. 16, 1926; Norw. Pat. 44,448, Oct. 10, 1927; Swiss Pat. 116,990, Oct. 1, 1926.

[3] Milligan, L. H., *J. Am. Chem. Soc.*, **44**, 567–70 (1922).

[4] Norsk Hydro-Elek. Kvael., Fr. Pat. 529,569, Dec. 1, 1921.

[5] Goldschmidt, V. M. and O. Ravner, U. S. Pat. 1,413,720, Apr. 25, 1922; Br. Pat. 125,578, Dec. 18, 1919; Fr. Pat. 520,988, July 5, 1921; Norw. Pat. 31,117, Sept. 27, 1920; Swed. Pat. 48,661, Mar. 2, 1921.

[6] Goldschmidt, H. J., U. S. Pat. 1,354,824, Oct. 5, 1920; Br. Pat. 113,276, June 13, 1918; Fr. Pat. 520,987, July 5, 1921; Ger. Pat. 339,983, Oct. 7, 1922; Norw. Pat. 29,275, Dec. 16, 1918; Swed. Pat. 45,116, Mar. 5, 1919; Swiss Pat. 90,698, Sept. 16, 1921.

See also Montecatini,Fr. Pat. 649,503, Dec. 24, 1928.

[7] Halvorsen, B. F., H. J. Falck, O. Ravner, U. S. Pat. 1,652,119, Dec. 9, 1927; Fr. Pat. 581,865, Dec. 8, 1924; Norw. Pat. 41,169, Apr. 6, 1925; Swed. Pat. 59,237, July 28, 1925.

The alkali nitrates are not decomposed at this temperature. By adding more potassium nitrate to the mixture,[1] the mass may be kept fluid and the formation of crusts avoided. This facilitates the maintenance of an even temperature throughout the mass and, consequently, the complete separation of alumina and alkalies. The heating may be accomplished by making the material a resistor in an electric furnace.[2]

To prevent the mass from fusing, alumina may be added to the mass, which is then heated to 100 to 130°C. in the presence of ammonia or other suitable base[3] and the alumina thus obtained in a form which is easy to filter. Part of the nitric acid may be recovered by distillation before the base is added. Crystals of aluminum nitrate without the potassium nitrate also may be decomposed by the action of ammonia gas.[4]

If the mixture of aluminum nitrate and alkali nitrate is calcined at higher temperatures, alkali aluminate is formed, but unless iron oxide be added,[5] the mixture tends to stick to the sides of the calciner and it is difficult to get a good formation of the aluminate. By leaching, the aluminate may be separated from the iron oxide and the solution treated in the usual way. Calcined alumina also may be used similarly to prevent aluminum nitrate crystals from sticking to the sides of the furnace during calcination.[6]

A recent British patent[7] states that aluminum nitrate can be advantageously decomposed by heating in vacuo with the addition of water or steam. It is preferred to use a basic nitrate, since this salt can be crystallized practically free from iron.

A basic calcium aluminum nitrate may be precipitated in the form of colorless needles by heating a solution containing calcium nitrate and aluminum nitrate with a certain amount of calcium oxide.[8] Basic aluminum nitrate may be crystallized out of a solution made with an excess of freshly precipitated aluminum hydroxide dissolved in 63 per cent nitric acid.[9]

Alumina also may be precipitated from a nitrate solution by heating with barium sulfide at 100 to 120°C.[10]

[1] HALVORSEN, B. F., U. S. Pat. 1,494,835, May 20, 1924; Fr. Pat. 556,766, July 26, 1923; Norw. Pat. 39,120, June 23, 1924.

[2] NORSK HYDRO-ELEK. KVAEL., Norw. Pat. 40,119, Nov. 3, 1924.

[3] FALCK, H. J. and T. MEJDELL, U. S. Pat. 1,507,993, Sept. 9, 1924. Fr. Pat. 548,034, Dec. 30, 1922; Norw. Pat. 38,053, Oct. 15, 1923.

[4] NORSK HYDRO-ELEK. KVAEL., Fr. Pat. 535,738, Apr. 20, 1922.

[5] HALVORSEN, B. F. and O. RAVNER, U. S. Pat. 1,523,807, Jan. 20, 1925; Fr. Pat. 556,765, July 26, 1923; Norw. Pat. 38,052, Oct. 15, 1923.

[6] NORSK HYDRO-ELEK. KVAEL., Fr. Pat. 559,576, Sept. 18, 1923.

[7] BUCHNER, M., Br. Pat. 283,117, Aug. 30, 1928.

[8] I. G. FARBENINDUSTRIE, A.-G., Ger. Pat. 443,568, May 2, 1927.

[9] FINKELSTEIN, H., Ger. Pat. 444,517, May 21, 1927.

[10] DAVIS, R. W., Jr., U. S. Pat. 1,321,013, Nov. 4, 1919.

CHAPTER VII

ELECTROTHERMAL AND MISCELLANEOUS FURNACE PROCESSES FOR THE PRODUCTION OF ALUMINA

By

Francis C. Frary, Junius D. Edwards and Ralph B. Mason

In addition to the alumina processes involving digestion with an acid or alkali, there is a group in which the first and characteristic step involves the use of a high temperature, generally in an electric furnace. In the simplest of these processes, the impurities are reduced to the metallic state and separated from the alumina; other processes convert the alumina into aluminum nitride, carbide, chloride, sulfide, etc. These furnace processes will be discussed in the present chapter.

"DRY PROCESS" ELECTROTHERMAL ALUMINA

While the chemical methods heretofore described, in so far as they have been successful, extract the alumina in aqueous solution and might be said to aim primarily at the production of a pure aluminum salt solution, by extracting the alumina from the ore and leaving most or all of the impurities insoluble, the "dry process" proceeds in the opposite direction by reducing the impurities to the metallic state and separating them from the molten pure alumina.

Aluminum Company of America Dry Process.

The simplicity of the dry process first appealed to Charles M. Hall,[1] and he and his company (Pittsburgh Reduction Company) spent several years and a large sum of money in

[1] Hall, C. M., U. S. Pats. 677,207; 677,208, June 25, 1901; Br. Pat. 14,572 (1900); Ger. Pat. 135,553, Nov. 4, 1902; Aust. Pat. 5983, Nov. 25, 1901; Norw. Pat. 10,181, Dec. 2, 1901.

Hall, C. M., U. S. Pat. 706,553, Aug. 12, 1902; Br. Pat. 2260 (1902) Mar. 13, 1902; Fr. Pat. 318,174, Oct. 8, 1902; Ger. Pat. 143,901, Sept. 7, 1903; Aust. Pat. 12,894, Aug. 10, 1903; Norw. Pat. 11,486, Jan. 12, 1903; Swed. Pat. 16,913, Jan. 9, 1904.

Hall, C. M., U. S. Pat. 677,209, June 25, 1901.

unsuccessful pioneer attempts to commercialize it. They were, however, unable to secure a sufficiently complete purification of the alumina for commercial purposes, and also unable to make the fused alumina behave properly in the electrolytic cells, so they were compelled to abandon it. However, a quarter of a century later their successors (Aluminum Company of America) solved both of these problems and put the process into commercial operation.[1] It is known that, in the interval, other aluminum companies had experimented with this process and in turn abandoned it, and although many other inventors had proposed modifications of Hall's original process and an extensive artificial abrasive industry (using fused alumina of 94 to 98 per cent purity) had developed, no one had previously been able commercially to produce aluminum from dry process alumina.

In the operation of the process, a mixture of ferruginous and siliceous bauxites, containing the proper proportions of iron, silicon, and titanium, is first sintered to remove water. There must be iron and silicon enough present to dissolve all the titanium after reduction and permit it to be tapped out as a ferrosilicon aluminum-titanium alloy. The sinter is then smelted in an electric furnace with the proper amount of coke to reduce all of the impurities and a little of the alumina.

The purity of the molten alumina may be tested by thrusting an iron bar into the body of the fused mass and allowing the alumina coating thereon to freeze in the air, whereby the surface exposed to the air acquires a color indicative of the purity of the alumina.[2]   A yellow color indicates about 1 per cent titanium,

[1] FRARY, F. C., U. S. Pat. 1,534,031, Apr. 21, 1925; Can. Pat. 256,131, Dec. 8, 1925; Fr. Pat. 600,146, Jan. 30, 1926; Ital. Pat. 238,676, July 8, 1925; Swiss Pat. 115,749, July 1, 1926.

HORSFIELD, B. T., Br. Pat. 248,360, Apr. 21, 1927; Fr. Pat. 622,313, May 28, 1927; Australian Pat. 1152, Dec. 14, 1926. Brazil Pat. 15,683, Nov. 13, 1926; Br. Guiana Pat. 199, July 3, 1926; Can. Pat. 277,526, Jan. 31, 1928; Hung. Pat. 92,647, Jan. 15, 1927; Indian Pat. 12,107, Jan. 24, 1927; Ital. Pat. 246,502, Mar. 30, 1926; Jap. Pat. 72,173, June 6, 1927; Mex. Pat. 25,736, Mar. 1, 1926; Rouman. Pat. 12,583, Feb. 22, 1926; Span. Pats. 97,214, 97,215, June 10, 1926; Swiss Pat. 121,105, July 1, 1927.

HORSFIELD, B. T., Br. Pat. 262,405, Jan. 19, 1928; Swiss Pat. 124,074, Jan. 2, 1928; Span. Pat. 100,681, Mar. 25, 1927; Ital. Pat. 254,680, Aug. 22, 1927; Indian Pat. 12,768, Aug. 29, 1927; Fr. Pat. 622,313; 1st Add. 32,581, Feb. 14, 1928.

[2] GABRIEL, L. W., U. S. Pat. 1,534,032, Apr. 21, 1925.

while a gray or black color indicates satisfactory elimination of titanium, iron, and silica, since the compounds of the last two are more easily reduced.

When 5 to 10 tons of molten purified alumina have been formed in the furnace, overlying a layer of the molten alloy containing the impurities, the furnace is tilted and the super-heated molten alumina poured off, at a temperature which is
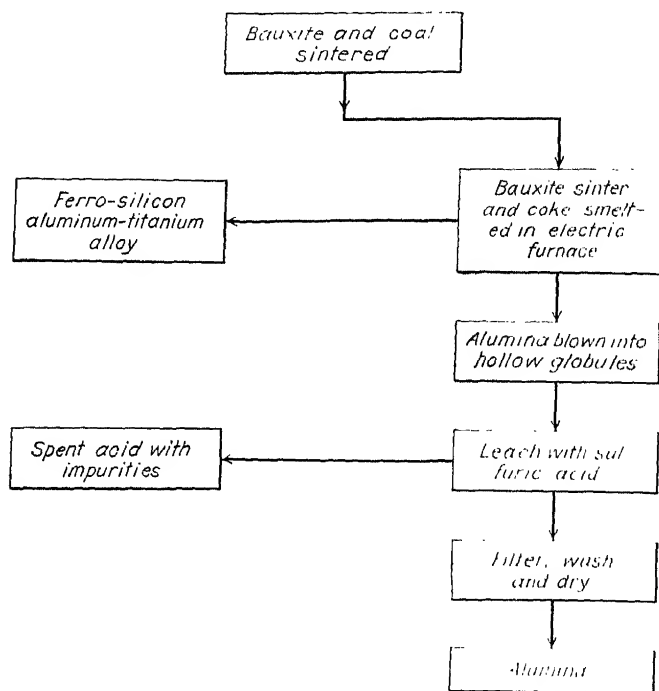
FIG. 44.—Diagram of Aluminum Company of America dry process for producing alumina.

probably about 2500°C. The alloy is later tapped out on the other side of the furnace.

The molten alumina may be cast into large blocks and subsequently crushed and ground to pass an 80-mesh screen, but a preferable procedure is to blow it into small hollow globules by the impact of a jet of high-pressure air or steam. In this process, the stream of molten alumina, as it issues from the tapping spout, meets the high-pressure blast from a nozzle located just below the spout. The alumina is blown into frag-

ments which are in the form of hollow globules ranging in size from very fine sand to $\frac{1}{8}$ or $\frac{3}{16}$ inch or more, with cellular walls, which as a rule do not exceed 0.01 inch in thickness and in most cases are much thinner. A part of the iron oxide remaining in the molten alumina is volatilized during the blowing operation, and all of the carbon and dissolved carbide is oxidized. If the velocity of the blast is too low, the larger globules may not be as completely oxidized as when a higher velocity is used,
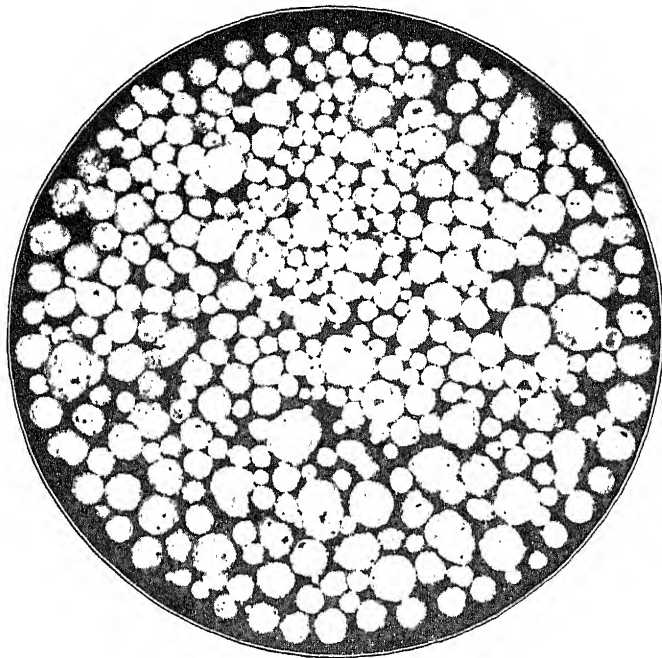
Fig. 15.   "Blown" alumina

and may contain larger amounts of iron and carbon. These larger globules are black in color, whereas the well-blown material is snow white. It is well known that by blowing blast furnace slag there is produced a fibrous material commercially known as "slag wool." This seems to be due to the viscous character-stics of silicate slags. When alumina substantially free from silica is blown in this way, however, there are produced the hollow globules just described.

The process is preferably completed by a leaching operation, in which the globular or pulverized alumina is treated with

dilute acid and washed to remove the lime (0.2 to 0.7 per cent, derived partly from the coke ash and partly from the bauxite) and about half of the remaining oxides of iron, silicon, and titanium. It is desirable to remove the lime because it accumulates in the electrolyte during the reduction process and, of course, the oxides of iron, silicon, and titanium are reduced with the alumina and contaminate the metal produced. As an example of the effect of leaching, ground alumina slag having an aluminum oxide content of 98.87 per cent was treated with a 10 per cent solution of sulfuric acid for 20 hours. After digestion and washing, the purity of the alumina was increased to 99.75 per cent. The digestion removed 60 to 65 per cent of the oxides of iron, silicon, and titanium present and substantially all of the lime. The resulting aluminum oxide is pure enough commercially to produce aluminum of 99.4 per cent purity.

Haglund Process.

The most important modification of the above described dry process is that due to Haglund,[1] and under development on a semi-commercial scale by the Vereinigte Aluminium Werke, at their plant in Lauta, Germany. The central idea of this modification is the reduction of the furnace temperature by lowering the fusing point of alumina. For this purpose, iron sulfide (*e.g.* pyrites) is included in the charge and sufficient carbon is employed to reduce all of the oxide impurities and an appreciable portion of the alumina. The alloy obtained is similar to that of the A. C. O. A. dry process, except for a high sulfur content, but the molten alumina contains 10 to 40 per cent of aluminum sulfide, which reduces the melting point of the slag at least 500°C. Haglund recommends the formation of a slag with about 20 per cent aluminum sulfide. Upon solidification, the aluminum oxide forms minute, transparent crystals imbedded

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[1] Haglund, T. R., U. S. Pat. 1,569,483, Jan. 12, 1926; reissue 17,001, June 19, 1928; Br. Pats. 232,549, Nov. 26, 1925; 234,830, Dec. 17, 1925; 289,639, May 3, 1928; 295,227, Aug. 2, 1928; Fr. Pats. 555,219, June 26, 1923; 598,378, Dec. 15, 1925; 599,559, Jan. 15, 1926; 624,796, July 26, 1927; 624,797, July 26, 1927; Ger. Pats. 449,930, Sept. 23, 1927; 451,523, Oct. 28, 1927; Aust. Pat. 105,346, Jan. 25, 1927; Norw. Pats. 40,531, Dec. 15, 1924; 44,304, Aug. 15, 1927; Swed. Pats. 56,713, May 27, 1924; 60,425, Mar. 23, 1926; Swiss Pats. 104,333, Apr. 16, 1924; 123,370, Dec. 16, 1927; Swiss Pat. 129,296, Dec. 1, 1928. Can. Pat. 282,064, July 31, 1928.

J. Ind. Eng. Chem., **18**, 67 8 (1926).

n a matrix of aluminum sulfide. Most of the impurities not 'educed to the metallic state are found in the matrix. Attention also should be called to the patent of Skappel[1] which deals with a similar process for separating ores and metallurgical products of all sorts, including fused sulfides and oxides, and to the Norton Company's proposal[2] to reduce the sulfide content to about 3 per cent.

To recover the alumina, the sulfide matrix is decomposed by water, steam, chlorine, or hydrochloric acid; the hydrogen sulfide produced is recovered as iron sulfide by absorption in ferruginous bauxite, preferably after a preliminary reduction of the iron to the ferrous state. The sulfurized bauxite is then used to supply part of the sulfur requirements in the furnace operation. If steam or water are used, the aluminum hydrate produced is separated by tabling, and the last traces removed from the alumina crystals by treatment with weak acid, after which it is dried. If chlorine or hydrochloric acid are used, the volatile chlorides of sulfur, iron, and titanium are formed. The latest and possibly the most practical procedure[3] consists in subjecting the fused melt of alumina and aluminum sulfide to incomplete oxidation so that at least part of the sulfur separates out as free sulfur. The temperature should be high enough to distill off the free sulfur, but not high enough to destroy the property of the alumina (from sulfide) to absorb water. The pure crystalline alumina can then be easily separated from the amorphous alumina and other impurities by means of water. The resulting alumina crystals are used like any other form of alumina in the electrolytic cell, or preferably mixed with aluminum oxide made by the Bayer process (see p. 310).

As early as 1907, Houdard[4] prepared crystals of alumina by heating alumina in a bath of molten aluminum sulfide.

Of the other inventors who have proposed improvements, Valatelli and Vialars[5] add nothing of importance to the original proposals of Hall. Gröppel[6] states that the major portion of the silica in basic aluminum silicates may be removed by smelting with aluminum or coal, the resulting product containing no more

[1] SKAPPEL, H., Norw. Pat. 43,940, Apr. 19, 1927.

[2] RIDGWAY, R. R., and J. B. GLAZE, U. S. Pat. 1,719,131, July 2, 1929.

[3] HAGLUND, T. R., Can. Pat. 282,065, July 31, 1928.

[4] HOUDARD, M., *Compt. rend.*, **144**, 1349 (1907).

[5] VALATELLI, G. and R. VIALARS, Fr. Pat. 525,097, Sept. 15, 1921.

[6] GRÖPPEL, K., *Metallurgie* **7**, 59–63 (1910). *C. A.* **5**, 853 (1911).

silica than the ordinary bauxite. Further purification would,
of course, be necessary. Sinding-Larsen[1] describes an impracti-
cal continuous process, in which aluminum silicate is fed into
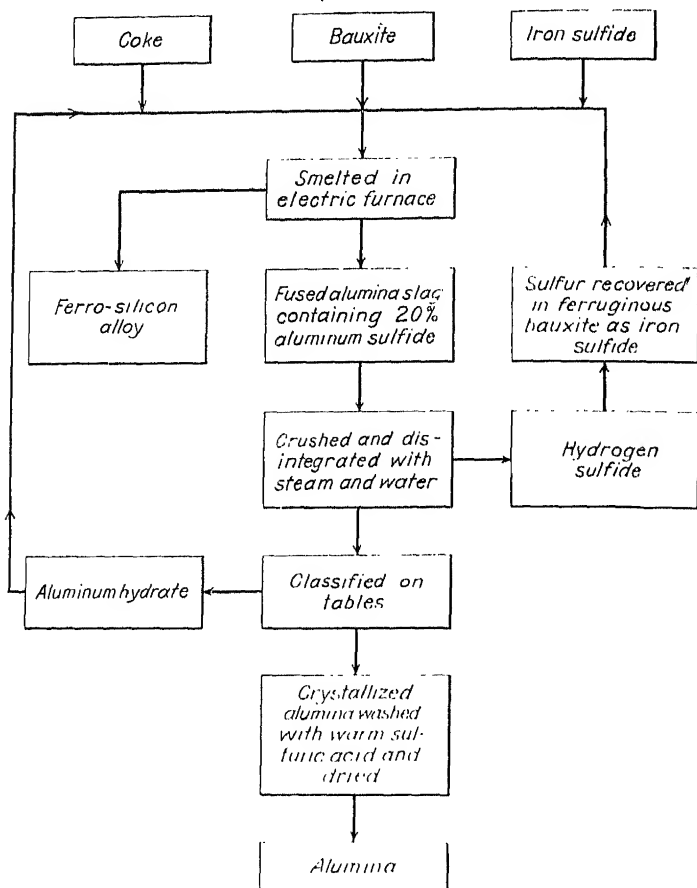
FIG. 46.   Diagram of Haglund process for producing alumina.

one end of a long electric furnace, while a mixture of iron, carbon,
and flux is fed into the opposite end. Tone[2] suggests the use of
manganese or a similar metal instead of iron, while Herren-

[1] SINDING-LARSEN, A., U. S. Pat. 927,758, July 13, 1909; Br. Pat. 25,408,
(1907), Nov. 16, 1908; Can. Pat. 109,512, Dec. 31, 1907; Swed. Pat. 27,370,
Aug. 21, 1909; Fr. Pat. 384,069, Mar. 28, 1908.

[2] TONE, F. J., U. S. Pat. 906,172, Dec. 8, 1908.

schmidt[1] proposes to add boric acid to the furnace charge. Hoy[2] uses calcium carbide to reduce molten aluminum silicate, forming alumina and calcium silicide, while Homan[3] prefers metallic aluminum as a reducing agent.

The Elektrizitätswerk Lonza[4] state that the aluminum (which has been formed by the reduction of alumina by carbon) present n the ferrosilicon can be utilized for the reduction of impurities n a fresh charge of material.

Tone[5] and Laur[6] propose to produce elementary silicon (which is lighter than molten alumina) instead of ferrosilicon, ut the high volatility of silicon at such temperatures and its ffinity for air would make such an operation impractical.

A process in which the carbon and alumina are added in the orm of briquettes and a reducing atmosphere maintained above he molten bath to prevent reoxidation of impurities has been ecently patented.[7]

The proposals of Weir,[8] Thomson,[9] and Seymour[10] to purify lumina by volatilization, need only be mentioned. Metallbank[11] as tried to improve the blowing process (see p. 238) by disinegrating the molten alumina with rotating discs and quenching he product in water.

[1] HERRENSCHMIDT, H., Br. Pat. 433 (1908), Jan. 7, 1909; Fr. Pats. 369,878, m. 23, 1907; 1st Add. 6834, Mar. 20, 1907; 2nd Add. 6839, Mar. 20, 1907; d Add. 8571, May 1, 1908; 4th Add. 8572, May 1, 1908; 5th Add. 8573, lay 1, 1908; 6th Add. 8815, July 4, 1908; 383,551, Mar. 12, 1908; Ger. Pats. 04,004, Nov. 4, 1908; 205,790, Jan. 3, 1909; Swiss Pats. 41,625, Jan. 8, 008; 42,566, Dec. 1, 1907.

[2] HOY, I., Norw. Pat. 28,212, Sept. 24, 1917.

[3] HOMAN, C. H., U. S. Pat. 732,410, June 30, 1903; Br. Pat. 6132 (1902) ine 12, 1903; Fr. Pat. 332,583, Oct. 31, 1903; Aust. Pat. 16,052, Apr. 25, 004.

See also HOOPER, L. D., Br. Pat. 217,376, June 19, 1924.

[4] ELEKTRIZITÄTSWERK LONZA, Fr. Pat. 640,057, July 5, 1928; Swiss Pat. 9,878, Jan. 2, 1929.

[5] TONE, F. J., U. S. Pat. 906,338, Dec. 8, 1908.

[6] LAUR, F., Fr. Pat. 125,277, June 7, 1911.

[7] ELEKTRIZITÄTSWERK LONZA, Fr. Pats. 640,737, July 20, 1928; 642,200, ug. 23, 1928.

[8] WEIR, F. C., Swed. Pat. 1848, Sept. 18, 1889.

[9] THOMSON, E., U. S. Pat. 1,450,464, Apr. 3, 1923.

[10] SEYMOUR, F. J., U. S. Pat. 382,273, May 1, 1888.

[11] METALLBANK u. METALLURGISCHE GES., Br. Pats. 277,640, Mar. 8, 28; 284,131, Jan. 26, 1928

Removal of Impurities in Fused Alumina.

After reduction with carbon, the metallic impurities do not always settle completely, and hence may contaminate the final product. The addition of sodium carbonate to the charge in the Hall process is said to increase the fluidity of the molten alumina, making it easier for the metallic impurities to settle.[1] If desired, the alkali aluminate formed during the fusion may be removed by treatment with water. A slight excess of carbon tends to produce carbides unless means are employed to prevent such formation. According to recent foreign patents,[2] a limited amount of carbon is added to the charge which is not quite enough to reduce all the impurities. Just before the molten mass is poured into water to granulate it, an excess of carbon and iron is added. Either metallic iron, ferrosilicon rich in iron, iron oxide, or a mixture of iron and aluminum oxides may be used for this purpose. The heavy molten iron absorbs the last traces of the lighter ferrosilicon suspended throughout the molten mass. Most of the unreduced impurities are dissolved in the aluminum carbide formed by the excess of carbon and are later leached out by means of dilute acid. Girod[3] substitutes bauxite for lime in the reduction of chrome iron ore in the electric furnace. The pure alumina which remains as a slag can be further purified by remelting in order that the last traces of the metallic impurities may settle.

According to Frenzel,[4] the alumina is melted in one furnace and then poured into a second, where a direct current is used to hasten the separation of the impurities. Machalske[5] proposes to fuse clay with carbon in an electric furnace and then subject the molten alumina to centrifugal action (!) to remove the impurities.

The addition of sufficient carbon to reduce all the impurities in bauxite results in the reduction also of some of the alumina. According to Saunders,[6] the addition of 10 to 20 per cent metallic

[1] ROCHETTE FRÈRES, Fr. Pat. 521,449, July 13, 1921.

[2] HÖGANÄS-BILLESHOLMS AKTIEBOLAG, Br. Pat. 252,693, applied for Apr. 27, 1926; Fr. Pat. 615,439, Jan. 7, 1927; Swiss Pat. 123,731, Dec. 16, 1927.

ELEKTRIZITÄTSWERK LONZA, Fr. Pats. 641,692, Aug. 8, 1928; 641,805, Aug. 11, 1928.

[3] GIROD, P., Fr. Pat. 344,549, Nov. 7, 1904.

[4] FRENZEL, F., Ger. Pat. 429,410, May 26, 1926.

[5] MACHALSKE, F. J., U. S. Pat. 1,062,982, May 27, 1913.

[6] SAUNDERS, L. E., U. S. Pat. 1,269,224, June 11, 1918.

ron makes it possible to reduce the impurities without reducing
the alumina. White[1] adds a substance, such as zinc oxide or
sodium carbonate, to the lower layer of the charge in a carbon-
hearth furnace to stop the formation of aluminum carbide.
Herrenschmidt[2] employs gases, such as carbon monoxide and
hydrogen, to reduce the impurities in molten alumina.

Saunders[3] purifies bauxites, etc., in the electric furnace by
using with an excess of carbon so as to produce aluminum
carbide with or without oxide. The reduced alloy is removed
and the carbide in the molten slag oxidized by means of an
oxidizing gas, such as air. Alternatively, the carbide impurity
may be oxidized by adding more fresh bauxite[4] or iron oxide[5]
to the heated alumina.

To eliminate silica from bauxite, Hall[6] fuses it with a fluoride,
such as cryolite or fluorspar. In connection with the Haglund
process, it should be noted that Richmond[7] mixes kaolin or
clay with pyrites and carbon and then fuses the material in an
electric furnace. The silicon sulfide formed by the reaction is
volatile and passes off along with the carbon monoxide. The
iron and alumina are separated as usual.

A French patent[8] states that fused alumina is hard to dissolve
in the electrolytic cells but by adding 5 to 10 per cent cryolite
or aluminum fluoride to the molten alumina before cooling, its
solubility in cryolite is increased and at the same time the iron
and silicon fluorides are eliminated as volatile compounds.
Higgins and Jeppson[9] treat the crushed fused alumina with a
boiling solution of sodium hydroxide and carbonate in order to

[1] WHITE, R. H., U. S. Pat. 1,269,141, June 11, 1918; Br. Pat. 118,606,
June 5, 1919; Fr. Pat. 491,024, May 19, 1919.

[2] HERRENSCHMIDT, H., Fr. Pat. 532,376, Feb. 2, 1922; 1st Add. 24,757,
Oct. 14, 1922; 2nd Add. 24,758, Oct. 14, 1922.

[3] SAUNDERS, L. E., U. S. Pat. 960,712, June 7, 1910; Can. Pat. 129,811,
Dec. 13, 1910.

[4] SAUNDERS, L. E., U. S. Pat. 1,269,223, June 11, 1918; Br. Pat. 118,605,
July 3, 1919; Ger. Pat. 382,741, Oct. 5, 1923; Norw. Pat. 31,322, Nov. 1,
1920; Swed. Pat. 47,046, May 26, 1920.

[5] DANNENBERG, E. A., Norw. Pat. 24,663, June 15, 1911.

[6] HALL, C. M., U. S. Pat. 678,732, July 16, 1901.

[7] RICHMOND, H. A., U. S. Pat. 1,245,383, Nov. 6, 1917.

[8] SOCIÉTÉ d'ELECTRO-CHIMIE ET d'ELECTRO-MÉTALLURGIE, Fr. Pat.
6,579, Apr. 22, 1921.

[9] HIGGINS, A. C. and G. N. JEPPSON, U. S. Pat. 944,436, Dec. 28, 1909;
Fr. Pat. 237,268, Aug. 2, 1911.

remove raw material not fully fused and impurities such as silicates. The purified material is used mainly for abrasives. According to Gerbel-Strover,[1] artificial abrasive grit (from bauxite fusions) is heated with sodium pyrosulfate (or sulfuric anhydride) to a temperature around 800°C. During the roasting operation, any carbon present is removed and the sodium in the pyrosulfate reacts with the silica to form a soluble compound. The metallic impurities in the form of sulfates are extracted by means of water. Other patents (Horsfield, see p. 239) have suggested the use of acids for extracting the impurities in fused alumina.

When the impure alumina is heated to 200°C. or above in the presence of chlorine or hydrochloric acid and a reducing agent, the silicon, iron, and ferrosilicon are changed to volatile chlorides, while the alumina remains behind.[2] The alumina may be treated in lump form and, as the gases penetrate this material, the resulting product becomes porous and brittle because of the removal of iron and silica, and is easily ground to a powder.

Purification of Alumina for Abrasives.

In the manufacture of abrasives, certain desirable products are made by using a fairly pure fused alumina. While in general the alumina thus used is not pure enough for the manufacture of metallic aluminum, yet the methods employed are very similar to those described under the dry processes for the preparation of alumina. No attempt will be made to cover the entire field of aluminous abrasives, but a brief survey of those processes producing relatively pure alumina will be made

Tone[3] heats a mixture of kaolin, carbon, and emery in an electric resistance furnace. The emery furnishes the iron which combines with the silicon to form an alloy. Allen[4] fuses calcined bauxite containing silica, iron, and titanium oxides as impurities with enough carbon to reduce the iron oxide and silica and only part of the titanium oxide. Hutchins[5] heats diaspore to drive off the combined water and then fuses it with a reducing agent in the electric furnace.

[1] Gerbel-Strover, E., Br. Pat. 10,328 (1915) June 8, 1916.

[2] Zaidan Hojin Rikagaku Kenkyujo, Br. Pat. 284,664, Oct. 29, 1928; Fr. Pat. 637,879, May 10, 1928; Swiss Pat. 129,877, Jan. 2, 1929.

[3] Tone, F. J., U. S. Pat. 929,517, July 27, 1909.

[4] Allen, T. B., U. S. Pat. 1,187,225, June 13, 1916.

[5] Hutchins, O., U. S. Pat. 1,326,595, Dec. 30, 1919

According to Davenport,[1] garnet dust is heated with carbon dust in the electric furnace to reduce the impurities and form ferrosilicon. For the complete removal of iron, it is sometimes necessary to add silica.

Hasslacher[2] melts a mixture of natural emery and carbon in an electric furnace to form iron and corundum. Tone[3] heats a mixture of emery ore and carbon in an electric furnace at a temperature below the reduction point of alumina but above the reduction point of silica. The electrodes are gradually raised and the purified alumina, being a poor conductor, remains at the bottom and solidifies.

In another patent, Tone[4] states that such substances as alunite may be heated in the electric furnace to a temperature in excess of 2000°C. to volatilize the potassium compounds. The iron and silicon also may be removed as ferrosilicon by adding carbon. According to Higgins,[5] the heating of alumina in the electric furnace to a temperature substantially above the temperature of quiet fusion avoids the segregation of impurities, carbides, etc.

To avoid having a too high conductivity in the charge, Tone[6] allows the reduction to take place in two stages, more carbon and iron oxide being added between the stages. Hutchins[7] fuses calcined bauxite with insufficient carbon to completely reduce all the impurities. The product is cooled and separated from the metallic impurities, and then used again with more carbon to reduce the silica, iron, and titanium oxides to less than 1 per cent. Only a small amount of carbon is necessary for this final fusion, as the carbon electrodes cause considerable reduction.

Richmond and Macdonald[8] fuse a natural corundum or impure alumina, containing not more than 0.6 per cent titanium, with carbon and metallic iron in the electric furnace to reduce most of the iron oxide and silica without reducing the titanium oxide. The amount of metallic iron necessary is about three times the quantity of silicon present in the material. Harrison[9] melts a mixture of diaspore, iron borings, and coke in the electric furnace and then allows the mass to cool slowly.

[1] Davenport, J., U. S. Pat. 1,192,394, July 25, 1916.

[2] Hasslacher, F., Br. Pat. 16,738 (1895), July 25, 1896; Ger. Pat. 85,021, Jan. 17, 1896.

[3] Tone, F. J., U. S. Pat. 1,002,608, Sept. 5, 1911.

[4] Tone, F. J., U. S. Pat. 1,239,984, Sept. 11, 1917.

[5] Higgins, A. C., U. S. Pat. 929,219, July 27, 1909.

[6] Tone, F. J., U. S. Pat. 929,518, July 27, 1909; Fr. Pat. 414,963, Sept. 1, 1910.

[7] Hutchins, O., U. S. Pat. 1,310,342, July 15, 1919; Br. Pat. 150,416, Sept. 2, 1920.

[8] Richmond, H. A. and R. Macdonald, Jr., U. S. Pat. 1,413,785, Apr. 5, 1922.

[9] Harrison, N. C., U. S. Pat. 1,314,061, Aug. 26, 1919.

Saunders[1] and Allen[2] prefer metallic aluminum to carbon for reducing the iron oxide and silica in molten alumina. The use of aluminum in place of carbon avoids the formation of aluminum carbide, which interferes with bonding the abrasive.

According to Gaçon,[3] a mixture of ferruginous bauxite, coke, and a flux, such as carbonate of calcium, potassium, or sodium, may be melted in an ordinary calcining furnace. Brockbank[4] first calcines bauxite or emery with sodium or potassium carbonate at 1100°C. in order to give easily fusible silicates. The material from the calciner is then mixed with sufficient coke to reduce the iron oxide and silica and fused in the electric furnace. After cooling, the product is crushed and treated with 10 per cent sulfuric acid for 6 hours at an elevated temperature. Richmond and Macdonald[5] state that an alkaline earth added to the charge of alumina, iron and carbon lowers the temperature of fusion, and also the viscosity of the molten mass.

Saunders and White[6] add a small amount of soda ash to the charge of bauxite and carbon in order to produce a weak grain in the product and to stop the reduction of the alumina. According to Allen,[7] the iron-titanium-silicon alloy is non-magnetic if there is less than 80 per cent iron present, and, consequently, certain quantities of this alloy remain in the fused alumina product. By heating the finely divided material with 3 to 5 per cent of substances which will readily give up oxygen at a high temperature, a ferroso-ferric-titano silicate is formed which is magnetic.

Claiming that the magnetic oxide of iron contained in fused alumina destroys the strength of molded and heated abrasives, Pettigrew and Gerbel-Strover[8] cool the fused alumina and, after breaking it up, heat the product in an oxidizing atmosphere to convert the magnetic oxide of iron into ferric oxide. Allen[9] heats the crushed abrasive at 800 to 1200°C. with a halogen salt of an alkali or alkaline earth metal to remove the carbides and silicides of iron, aluminum, and titanium.

[1] SAUNDERS, L. E., U. S. Pat. 954,768, Apr. 12, 1910.

[2] ALLEN, T. B., U. S. Pat. 1,448,586, Mar. 13, 1923.

[3] GAÇON, A., Fr. Pat. 332,770, Nov. 6, 1903.

[4] BROCKBANK, C. J., U. S. Pat. 1,402,714, Jan. 3, 1922.

[5] RICHMOND, H. A. and R. MACDONALD, JR., U. S. Pat. 1,583,179, May 4, 1926.

[6] SAUNDERS, L. E., and R. H. WHITE, U. S. Pat. 1,263,710, Apr. 23, 1918; Br. Pat. 118,592, Mar. 7, 1919; Ger. Pat. 382,684, Oct. 5, 1923; Norw. Pat. 32,370, May 30, 1921.

[7] ALLEN, T. B., U. S. Pat. 1,199,041, Sept. 26, 1916.

[8] PETTIGREW, J. and E. GERBEL-STROVER, Br. Pat. 8,483 (1914), July 1, 1915.

[9] ALLEN, T. B., U. S. Pat. 1,001,572, Aug. 22, 1911; Fr. Pat. 432,503, Dec. 8, 1911.

The excess of halide salt is removed by washing. Kalmus[1] prepares pure alumina from nepheline-syenite by means of sulfur dioxide solution and then fuses the pure alumina either alone or mixed with other oxides to make a crystalline abrasive product.

Higgins[2] roasts the fused abrasive material to oxidize carbon and carbides. According to Saunders and White,[3] a volatile oxygen compound of sodium or zinc may be added to the fused alumina to prevent the formation of carbides. Tone and Allen[4] remelt the fused alumina with oxide of iron to destroy carbides or suboxides of aluminum. Tone[5] states that the addition of sufficient carbon to cause the complete reduction of titanium oxide causes the formation of carbides. By adding iron oxide or other oxidizing agents[6] to the fused mass, or fusing a second time with these reagents, the carbides are destroyed. Vierheller[7] adds iron filings to fused alumina to increase the density of the impurities (especially silicon), an oxidizing agent, such as manganese dioxide, barium peroxide, potassium chlorate, or potassium nitrate, to oxidize carbides, and a gas-producing compound, such as sodium carbonate or ammonium chloride, to promote thorough mixing and thus hasten the settling of the impurities. Brockbank[8] claims that a more complete reduction of aluminous ores can be obtained, more carbon may be added without the formation of carbides, and the impurities are more easily removed if boric acid is present. For the preparation of refractory material, Lecesne[9] mixes bauxite and anthracite in suitable proportions to form aluminum carbide, and burns the mixture in a furnace through which air under pressure is conducted in order to burn up the excess anthracite and carbide.

Pettigrew and Gerbel-Strover[10] allow the molten alumina to cool slowly in a vacuum, while Kalmus[11] allows it to cool in thin streams, preferably directing a cooling gas upon the slender stream as it falls upon the moving mold, to secure rapid cooling. Higgins[12] chills the pig of fused alumina by directing a stream of water against the

[1] KALMUS, H. T., U. S. Pat. 1,234,905, July 31, 1917.

[2] HIGGINS, A. C., U. S. Pat. 930,376, Aug. 10, 1909; Can. Pat. 120,857, Sept. 28, 1909.

[3] SAUNDERS, L. E. and R. H. WHITE, U. S. Pat. 1,269,222, June 11, 1918.

[4] TONE, F. J., and T. B. ALLEN, U. S. Pat. 1,044,296, Nov. 12, 1912.

[5] TONE, F. J., U. S. Pat. 1,276,134, Aug. 20, 1918; Fr. Pat. 489,314, Jan. 2, 1919.

[6] HERRENSCHMIDT, H., Fr. Pat. 384,493, Apr. 10, 1908.

[7] VIERHELLER, H., Ger. Pat. 422,105, Mar. 24, 1925.

[8] BROCKBANK, C. J., U. S. Pat. 1,568,873, Jan. 5, 1926.

[9] LECESNE, N., Br. Pats. 102,507, Dec. 3, 1917; 124,208, May 26, 1921.

[10] PETTIGREW, J. and E. GERBEL-STROVER, Ger. Pat. 268,930, Jan. 7, 1914.

[11] KALMUS, H. T., U. S. Pats. 1,149,064, Aug. 3, 1915; 1,226,892, May 22, 1917.

[12] HIGGINS, A. C., U. S. Pat. 916,866, Mar. 30, 1909.

outside steel shell of the furnace. Hutchins[1] states that the molten material may be quenched by a stream of water as it issues from the furnace, a porous product with relatively small crystal size being obtained. According to Saunders and White,[2] an abrasive whose crystals are perforated or cellular may be obtained by adding alkali metal salts or substances, such as aluminum fluoride, zinc, or zinc oxide, which are capable of existing in the vapor phase just before the alumina solidifies.

x   ALUMINUM NITRIDE PROCESS

In any survey of the commercial processes for the production of alumina, consideration must be given to a discussion of the nitride process. Much time and effort have been spent upon the investigation of aluminum nitride, an interesting product of the electric furnace, which is an intermediate compound in the fixation of atmospheric nitrogen and the production of alumina suitable for use in the aluminum industry. Semi-commercial work on this process was carried on over a period of years by Société Générale des Nitrures (owners of the Serpek patents), Aluminum Company of America, Armour and Company, and others. The process is not economical for the aluminum industry, unless the by-product ammonia can be made to yield considerable revenue and hence reduce the cost of the alumina. Bauxite is used in the production of aluminum nitride, and it would be much cheaper to extract the alumina directly from the bauxite instead of from the nitride if it were not for the ammonia. Several other factors, such as ease of extraction, removal of silica, etc., must be considered, as well as the difficulties involved in the nitrification of the original charge. Even before the recent commercialization of cheaper synthetic ammonia processes, such as that of Haber, completely destroyed any possibility which the nitride process had of competing with the Bayer process, inherent difficulties caused its abandonment.

The history of aluminum nitride is more recent than that of aluminum itself, since the compound was first prepared and identified by Briegleb and Guether[3] in 1862, when they heated metallic aluminum, containing silicon and iron, to a high tempera-

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[1] HUTCHINS, O., U. S. Pat. 1,524,134, Jan. 27, 1925.

[2] SAUNDERS, L. E. and R. H. WITTE, U. S. Pat. 1,263,709, Apr. 23, 1918; Br. Pat. 118,591, May 15, 1919; Ger. Pat. 371,677, Mar. 17, 1923; Norw. Pat. 32,369, May 30, 1921.

[3] BRIEGLEB AND GUETHER, *Ann.*, **123**, 238 (1862).

ture in a stream of nitrogen, and then decomposed the compound
by fusion with potash to obtain ammonia. The reaction
between metallic aluminum and nitrogen is exothermic after
it is once started, and this no doubt explains the fact that the
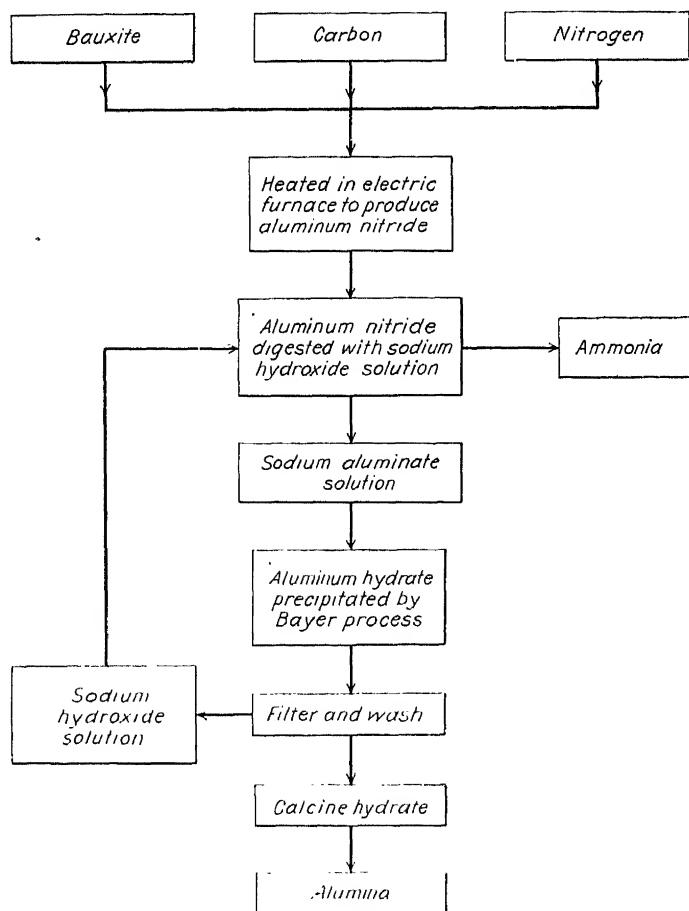
FIG. 47.   Diagram of Serpek process for producing alumina.

arly experimenters used the metal to obtain the nitride.   While
he formation of the nitride from the metal is interesting from
scientific standpoint, a commercial process must, of course,
se alumina as the raw material.

When alumina, carbon, and nitrogen are heated to a very
igh temperature, nitrogen is absorbed and aluminum nitride

and carbon monoxide are formed. Although the reaction between metallic aluminum and nitrogen is exothermic, as stated above, the extremely high heat of formation of aluminum oxide makes the reaction just mentioned highly endothermic. According to the Serpek patents, a temperature around 1800°C. is required for satisfactory operation. In order to obtain such a temperature, it is necessary to use electric heat, and the development of the nitride process has largely hinged on the development of a suitable electric furnace. The difficulties of operation are apparently increased by the fact that there appears to be an upper temperature limit (about 2200°C.) above which the nitrification does not take place, and where aluminum carbide is the stable phase.

Physical Chemistry of Aluminum Nitride Reactions.

Considerable difficulty has been encountered in the experimental determination of the heat of formation of aluminum nitride, because of the fact that the combustion of the compound is incomplete in the calorimeter and it is not surprising, therefore, that the results show wide variations. The heat of formation of aluminum nitride in the original determination by Fichter[1] was found to be 27,369 calories, but this value is much too low. A later determination by Fichter and Jenny[2] gives a value of 62,000 calories, and this is, without doubt, more nearly correct. Richards[3] uses a value of 45,450 calories for the heat of formation, while Matignon[4] states that it is 55,000 calories. The latest estimate is that of Prescott and Hincke,[5] who calculate from equilibrium measurements, a value of 80,434 calories.

As was mentioned above, the reaction

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$
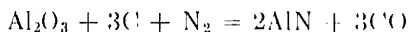
is highly endothermic and various negative heat values have been assigned to it. Richards[6] estimates that the reaction requires 213,220 calories, Fraenkel[7] 243,000 calories, Matignon[8]

[1] Fichter, F., *Z. anorg. Chem.*, **54**, 322-327 (1907).

[2] Fichter and Jenny, *Helvetica Chim. Acta.*, **5**, 448-51 (1922).

[3] Richards, J. W., *Trans. Am. Electrochem. Soc.*, **23**, 356 (1913).

[4] Matignon, C., *Chem. Ztg.*, **38**, 894-5, 909-10 (1914).

[5] Prescott, Jr., C. H., W. B. Hincke, *J. Am. Chem. Soc.*, **50**, 3228 (1928).

[6] *Loc. cit.*

[7] Fraenkel, W., *Z. Elektrochem.*, **19**, 362-373 (1913).

[8] *Loc. cit.*

187,600 calories, and Krase, Thompson, and Yee[1] 168,720 calories. Moldenhauer[2] has calculated, by means of the Nernst heat theorem, the value 189,000 calories at 1500°C. from the approximate equilibrium measurements of Fraenkel, while Prescott and Hincke find a value of 138,711 calories.

According to the experiments of Fraenkel, the rate of the reaction increases rapidly with temperatures from 1300 to 1600°C. The amount of nitrogen fixed in ½ hour was 3.1 per cent at 1400°C., 4.4 per cent at 1450°C., 8 per cent at 1500°C., 9.5 per cent at 1550°C., and 24.5 per cent at 1600°C. The last value given does not indicate the rate of the reaction, when compared with the other values, since at this temperature the major part of the reaction is over in ½ hour. At 1500°C., experiments showed that the yields are proportional to the time.

The experiments of Fraenkel have also shown that the reaction is reversible and that, especially at the lower temperatures, the presence of a large excess of carbon monoxide will stop the reaction and even decompose aluminum nitride into alumina and nitrogen. At a temperature of 1500°C. and a pressure of 1 atmosphere, the equilibrium concentration is between 25 and 30 per cent carbon monoxide by volume, and at 1600°C. between 60 and 65 per cent by volume. In two tests at 1700°C., a lively nitrification was produced when there was 70 per cent carbon monoxide by volume present. These experiments demonstrate that a relatively high proportion of carbon monoxide may be present in the nitrogen, provided a higher temperature is used.

The measurements of Prescott and Hincke indicate that for a total pressure of 1 atmosphere the equilibrium mixture contains 1.6 per cent carbon monoxide at 1500°C., and 66 per cent at 1600°C.

The sublimation and consequent decomposition of aluminum nitride takes place at extremely high temperatures, and the extent of the decomposition is dependent on the pressure of the nitrogen. Working at atmospheric pressure, Tucker and Read[3] found that the decomposition starts around 2000°C.,

[1] KRASE, H. J., J. G. THOMPSON, and J. Y. YEE, *J. Ind. Eng. Chem.*, **18**, 288 (1926).

[2] MOLDENHAUER, W., "Die Reactionen des freien Stickstoffs," Borntraeger, Berlin, (1920).

[3] TUCKER, S. A. and H. L. READ, *Trans. Am. Electrochem. Soc.*, **22**, 57 (1912).

while Wolf[1] states that the sublimation begins around 1850°C. If the pressure of the nitrogen is reduced to 14 millimeters of mercury, Fichter and Oesterheld[2] find that the sublimation and decomposition begin at 1870°C. ± 20°C. Wolf has determined the melting point of aluminum nitride to be between 2150°C. and 2200°C. under a pressure of 4.3 atmospheres of nitrogen. Matignon[3] states that aluminum nitride does not melt at 2200°C. The crystalline form of aluminum nitride is less reactive than the amorphous form produced at lower temperatures.

Fichter and Spengel[4] have described certain chemical properties of aluminum nitride. Aluminum nitride is decomposed slowly by alkali solutions, but rapidly by molten alkali, yielding ammonia and alkali aluminate. Acids also decompose the compound, forming aluminum and ammonium salts of the acid. For example, the reaction between aluminum nitride and gaseous hydrochloric acid[5] produces aluminum and ammonium chlorides. For the quantitative determination of nitrogen, the method of Kjeldahl is recommended. Aluminum nitride is not acted upon by hydrogen. The dry halogens react only slowly, even at high temperatures. Aluminum nitride reacts with air noticeably at 760°C. and, after heating for 4 hours at 830° to 840°C., it was found that the residue contained only 8 per cent nitrogen. Potassium dichromate and other strong oxidizing agents decompose the compound. However, potassium nitrate, potassium chlorate, potassium permanganate, and copper oxide are without much action. Aluminum nitride heated to 1220°C. in a stream of nitrogen was not attacked by carbon, but aluminum carbide reacted with nitrogen slightly at 1200°C. Carbon monoxide does not react with aluminum nitride at 1100°C., but carbon dioxide reacts noticeably at 1120°C. with this compound, and after 1½ hours at 1140°C., 54.14 per cent is oxidized, and at 1300°C., 89 per cent is oxidized.

Conversion of Carbide into Nitride.

The chemistry of high-temperature reactions is not always apparent and, considering the difficulty of working at tem-

[1] WOLF, J., *Z. anorg. Chem.*, **87**, 120–128 (1914).

[2] FICHTER, F., G. OESTERHELD, *Z. Elektrochem.*, **21**, 50 (1915)

[3] MATIGNON, C., *Compt. rend.*, **177**, 1290–1293 (1923).

[4] FICHTER, F., A. SPENGEL, *Z. anorg. Chem.*, **82**, 192–203 (1913.)

[5] MONTEMARTINI, C., L. LOSANA, *Giorn. chim. ind. applicata*, **6**, 323–325 (1924).

)eratures around 2000°C., it is not surprising that the earliest :onclusions were incorrrect and later abandoned.

The earliest patents to Serpek deal with the nitrification of iluminum carbide. It was assumed that when a mixture of ilumina, carbon, and nitrogen was heated to a high temperature n the electric furnace, the first reaction was a reduction of the ilumina by the carbon, resulting in the formation of aluminum :arbide. The reaction between the carbide and nitrogen was hen supposed to take place with the formation of nitride. In he early patents to Serpek,[1] aluminum carbide is heated to
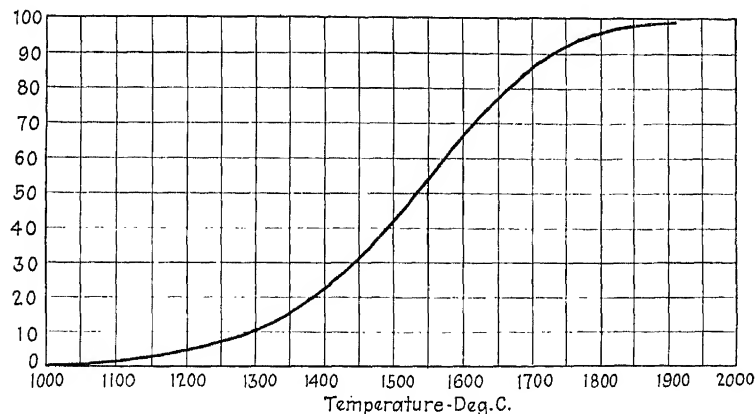
ı(ı. 48.---Equilibrium curve for nitride formation from alumina, carbon and nitrogen; per cent of carbon monoxide as a function of temperature.

high temperature in an atmosphere of nitrogen. Carbon and lumina or aluminum chloride may be added to dilute the ırbide and increase the nitrogen adsorption. The addition f hydrochloric acid gas or sulfur dioxide to the nitrogen is said) speed up the reaction. The metals copper, aluminum, and on, or their alloys, are likewise said to be catalysts for the ·action.

In later patents,[2] some carbide is formed directly in the ırnace by heating alumina and carbon to a high temperature

[1] SERPEK, O., U. S. Pat. 867,615, Oct. 8, 1907; Br. Pat. 13,579 (1906) ·b. 7, 1907; Fr. Pat. 367,124, Oct. 20, 1906; Ger. Pats. 181,911, Mar. 1,)07; 235,213, June 2, 1911; 235,669, June 19, 1911; 181,992, Mar. 2, 1907; ın. Pat. 102,653, Dec. 18, 1906.

[2] SERPEK, O., Br. Pat. 15,995 (1909), Nov. 18, 1909; Fr. Pat., 1st Add. to ·7,124 -12,482, Sept. 23, 1910; Ger. Pats. 183,702, Apr. 11, 1907; 231,886, ·b. 28, 1911; Swiss Pat. 43,474, Nov. 11, 1908.

and then nitrogen is blown through the mass. The second reaction is supposed to be exothermic. Fujiyama[1] burns the carbide in air and then, after a suitable temperature is developed, nitrogen is conducted into the reaction chamber. Another batch of carbide is introduced and the procedure repeated. Hershman[2] heats a mixture of alumina and carbon (1 mol Al_2O_3 to 6 atoms C) with 0.5 to 5.0 per cent of a carrying agent, such as titanium or calcium compounds, to a temperature of 1500°C., in a current of water gas, to form mainly carbides. The mixture of carbon monoxide and hydrogen is supposed to be more reactive than either one alone. By heating the product with carbon dioxide, more reactive subcarbides or metals are supposed to form. These are then heated to 1500 to 1600°C. in a current of nitrogen or a mixture of nitrogen and hydrogen, to form the nitrides. Barnett and Burgess[3] state that aluminum nitride is produced by heating aluminum carbide in an atmosphere of nitrogen at a temperature of 900 to 1200°C., while Hershman[4] states a temperature of 1700 to 1800°C. is adequate, provided there is present 0.1 per cent of a catalytic agent, such as boron, titanium, or their compounds. The addition of carbonaceous material is beneficial and calcium oxide is supposed to aid the reaction by destroying carbon monoxide.

According to Moissan,[5] aluminum carbide does not react with nitrogen at red heat. Fichter[6] states that the aluminum carbide made at a very high temperature does not readily react with nitrogen and that there was no reaction at 1200°C. The experiments of Krase, Thompson, and Yee[7] show that crude aluminum carbide is only partially nitrified at 1100°C. in 15 minutes, 17.31 per cent of the aluminum changing to nitride.

Prescott and Hincke[8] find that for the reaction

$$4AlN + 3C = Al_4C_3 + 2N_2$$
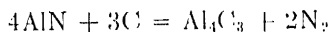
the heat of reaction is 261,478 calories. At 1600°C. the equilib-

[1] Fujiyama, T., U. S. Pat. 1,126,000, Jan. 26, 1915.

[2] Hershman, P. R., U. S. Pats. 1,188,771; 1,188,772, June 27, 1916.

[3] Barnett, M. and L. Burgess, U. S. Pat. 1,252,649, Jan. 8, 1918.

[4] Hershman, P. R., U. S. Pats. 1,188,769; 1,188,770, June 27, 1916.

[5] Moissan, *Compt. rend.*, **119**, 16–20 (1894).

[6] Fichter, F., *Extract Arch. sci. phys. nat.*, **35**, 369–381 (1913).

[7] Krase, H. J., J. G. Thompson, and J. Y. Yee, *J. Ind. Eng. Chem.*, **18** 1288 (1926).

[8] *Loc. cit.*

ium pressure of nitrogen is 0.01 millimeter; at about 2525°C.
he equilibrium pressure of nitrogen is 1 atmosphere.

Aluminum Nitride from Alloys.

Serpek soon gave up the idea of making aluminum nitride
rom the carbide. The reaction between aluminum carbide and
nitrogen is explained by Caro[1] as follows: By the action of heat,
he aluminum carbide is decomposed into aluminum and carbon,
and the nitrogen then combines with the aluminum. In general,
more nitrogen combines with aluminum carbide at 1150°C. if
metallic aluminum is present than combines with pure carbide,
nd the largest yield comes when pure aluminum is used. Very
little nitrogen combines with the pure carbide, as at the above
temperature the dissociation of the carbide is small.

If the formation of aluminum nitride is dependent upon the
reaction between nitrogen and the free metal, other methods
an be used to better advantage. Apparently after meeting
with difficulties in the carbide method, Serpek attacked the
problem in a slightly different way. A powdered mixture of
alumina (3 parts), carbon (1 part), and a metal (5 per cent),
uch as iron or copper, which is capable of forming an alloy with
aluminum, is heated in an atmosphere of nitrogen to a high
temperature.[2] The alumina is reduced by the carbon, and the
aluminum alloys itself with the iron or copper. The reaction
etween the aluminum and nitrogen is exothermic and, after
he alloy is formed, less external heat is required. The catalytic
influence of chlorine and sulfur dioxide upon the reaction is
gain mentioned. In another method,[3] iron is melted in an
electric furnace and supersaturated with carbon. Alumina and
arbon are added while the bath is kept in circulation with
roducer gas. A possible explanation for the reaction is that
he metallic aluminum, formed by the reduction of the alumina
with carbon, alloys with the iron and then reacts with the
nitrogen in the producer gas to form aluminum nitride.

Making use of the exothermic nature of the reaction between
ferro-aluminum and nitrogen, Serpek[4] heats a mixture of

[1] CARO, N., *Z. angew. Chem.*, **23**, 2405–2417 (1909).

[2] SERPEK, O., U. S. Pat. 888,044, May 19, 1908.

[3] SERPEK, O., Br. Pat. 15,996 (1909), Oct. 14, 1909; Fr. Pat. 415,216, Sept.
1, 1910; Ger. Pat. 216,746, Nov. 30, 1909.

[4] SERPEK, O., U. S. Pat. 1,155,840, Oct. 5, 1915; Fr. Pat. 474,330, Feb.
7, 1915; Ger. Pat. 367,767, Jan. 25, 1923.

ferro-aluminum, bauxite, and carbon to a temperature of 1200°C. in an atmosphere of nitrogen. The temperature rises to about 1850°C. and then slowly falls, remaining for 5 hours above 1500°C. In a later patent[1] he mentions the use of catalytic bodies, such as oxides, sulfates, aluminum fluoride, or aluminum carbide. The aluminum-iron alloy also may be treated[2] with nitrogen at 1250 to 1300°C. in a Bessemer type of furnace, thus saving a second heating. Silicon and titanium are said to assist in the fixation of nitrogen.

Badin[3] heats a mixture of carbon and bauxite containing 30 to 60 per cent iron in the electric furnace. The resulting iron-aluminum alloy is finely divided, moistened, and exposed to the air. A temperature of 2000°C. is said to develop without the addition of external heat and the aluminum combines with pure nitrogen or the nitrogen of the air. Bunet[4] states that more nitrogen is fixed if calcium carbide is added to the ferro-aluminum.

Gerber[5] heats alumina or aluminum silicate with carbon in the presence of iron. Most of the impurities volatilize or combine with the iron to form an alloy. The molten alumina is treated with nitrogen and a reducing agent to form the nitride, electric energy being used to supply the necessary heat for the reaction.

Krase, Thompson, and Yee (*loc. cit.*) experimented with the production of ferro-aluminum alloys by the reduction of iron ore and low-grade bauxite with carbon in the electric furnace, and obtained alloys containing 5 to 50 per cent aluminum. The nitrification experiments showed that metallic calcium and titanium in the ferro-aluminum alloy decrease, while magnesium increases, the amount of nitrogen actually combined. Moistening the alloy with water, or adding hydrogen to the nitrogen

[1] SERPEK, O., U. S. Pat. 1,198,965, Sept. 19, 1916; Br. Pat. 27,971(1913) Aug. 7, 1914; Fr. Pats. 474,322, Feb. 17, 1915; 170,099, Aug. 20, 1911; 1st Add. 19,862, Oct. 7, 1915; Ger. Pat. 360,038, Sept. 29, 1922.

[2] Soc. Gén. des Nitrures, Fr. Pat. 470,099, Aug. 20, 1911; Br. Pat. 27,030 (1913) Apr. 2, 1914.

[3] BADIN, A., U. S. Pat. 1,196,639, Aug. 29, 1916; Fr. Pat. 174,365, Feb. 18, 1915; 1st Add. 19,863, Oct. 7, 1915; Br. Pat. 22,586 (1914), Feb. 11, 1915.

[4] BUNET, P., U. S. Pat. 1,196,657, Aug. 29, 1916; Br. Pat. 28,071 (1913), Feb. 26, 1914; Fr. Pat. 476,121, July 13, 1915.

[5] GERBER, V., U. S. Pat. 1,350,149, Aug. 17, 1920; Br. Pat. 139,195, Mar. 31, 1921; Ger. Pat. 343,793, Nov. 10, 1921.

aused a decrease in the nitrogen absorption. Practically complete nitrification of the aluminum in the alloy can be obtained if a small quantity of chloride or fluoride of an alkaline earth metal or aluminum be added to the alloy before it is nitrified.

According to Hershman,[1] aluminum skimmings are heated with carbon in a closed retort to 1200°C. and then quickly exposed to the air. The temperature rises and aluminum nitride is formed. Sulfur (or sulfur compounds) is said to catalyze the reaction between metallic aluminum, carbon and nitrogen.[2]

Giulini[3] claims that if metallic sodium vapors are used as the reducing agent instead of carbon, the reaction between alumina and nitrogen will take place at a lower temperature, an electric furnace not being required. It is not necessary to add metallic sodium, as it can be generated directly in the furnace by the reduction of sodium carbonate or oxide with carbon.

Aluminum Nitride from Alumina, Carbon, and Nitrogen.

The production of aluminum nitride from aluminum carbide or aluminum alloys not being commercially successful, another slightly different process was finally brought out. After considerable experimentation, Serpek found that aluminum nitride could be made by heating alumina and carbon in an atmosphere of nitrogen at a temperature around 1800°C. or even lower, a noticeable reaction taking place at 1100°C. These temperatures are so low that the formation of aluminum carbide or aluminum in an atmosphere of nitrogen would be impossible.[4]

An earlier patent to Willson[5] states that metallic nitrides may be prepared by heating the oxide of the metal with carbon and nitrogen in the electric furnace. The example given in

[1] HERSHMAN, P. R., U. S. Pat. 1,229,611, June 12, 1917.

[2] SERPEK, O., Fr. Pat. 426,868, July 20, 1911.

[3] GIULINI, G., U. S. Pat. 1,180,840, Apr. 25, 1916; Fr. Pat. 451,405, Apr. 8, 1913; Ger. Pat. 295,573, July 2, 1919; Swiss Pat. 62,849, Nov. 8, 1912; Br. Pat. 25,874 (1912), Aug. 21, 1913; Norw. Pat. 27,618, Feb. 5, 1917.

[4] SERPEK, O., U. S. Pat. 987,408, Mar. 21, 1911; Br. Pat. 7507 (1909) Jan. 20, 1910; Can. Pat. 134,728, Aug. 1, 1911; Fr. Pat. 411,031, June 6, 1910; Ger. Pat. 224,628, July 21, 1910; Swed. Pat. 28,761, Apr. 30, 1910; Swiss Pat. 48,470, May 18, 1909.

[5] WILLSON, T. L., Br. Pat. 21,755 (1895), Sept. 19, 1896.

the patent is for magnesium nitride, but aluminum nitride is also mentioned.

Furnaces.

Many difficulties were encountered in attempting the commercial operation of this process. For example, the furnace linings break down at the very high temperatures necessary for successful operation. Serpek suggested the use of aluminum nitride itself as a furnace lining, although carbon or graphite is usually mentioned. The reaction itself requires a large amount of heat, and for economical operation the reacting substances should be preheated. The spent gases coming from the reaction zone are usually used to preheat the solid material as it slowly passes through the furnace, and the hot aluminum nitride is utilized to heat the nitrogen or nitrogen-containing gases which are traveling in the opposite direction to the flow of solid material.[1] According to Sigrist,[2] it is advantageous to have the hottest nitride in contact with the concentrated nitrogenous gases, since aluminum nitride does not decompose in the presence of pure nitrogen.

The reaction between alumina, carbon, and nitrogen is (erroneously) supposed to take place very rapidly at a high temperature, and various patents have described processes in which the finely divided material is projected through an electric arc or over resistance elements in the presence of nitrogen,[3] or through a flame produced by the combustion of an excess of carbon in air, with the production of almost exclusively carbon monoxide.[4] If the temperature of the flame is not high enough,

[1] SERPEK, O., U. S. Pat. 996,032, June 20, 1911; Can. Pat. 131,684, Apr. 28, 1913; Br. Pats. 13,086 (1910), Feb. 23, 1911; 23,544 (1911), Feb. 29, 1912; 22,435 (1912), Jan. 23, 1913; Ger. Pat. 239,909, Oct. 30, 1911; Fr. Pats. 430,822, Oct. 25, 1911; 427,109, July 27, 1911; 1st Add. 17,215, July 26, 1913; 2nd Add. 18,866, July 27, 1914.

COUTAGNE, G., Fr. Pat. 462,462, Jan. 28, 1914.

DUNCAN, H. L., U. S. Pat. 1,241,834, Oct. 2, 1917

[2] SIGRIST, J., Fr. Pat. 543,529, Sept. 5, 1922.

[3] SERPEK, O., U. S. Pats. 1,217,842, Feb. 27, 1917; 1,233,925, July 17, 1917; 1,212,119, Jan. 9, 1917; Br. Pat. 24,731 (1913), Mar. 12, 1914; Fr. Pat. 478,886, Jan. 14, 1916; Swed. Pat. 41,510, Nov. 1, 1916; Swiss Pat. 71,804, Feb. 16, 1916.

SOC. GÉN. DES NITRURES, Br. Pat. 23,740 (1913), Apr. 30, 1914.

[4] SERPEK, O., U. S. Pat. 1,233,926, July 17, 1917; Br. Pat. 24,533 (1914), Mar. 4, 1915; Fr. Pat. 488,554, Oct. 21, 1918; Norw. Pat. 27,528, Jan. 8, 1917; Swiss Pat. 74,225, Feb. 1, 1917.

BADIN, A., U. S. Pat. 1,143,482, June 15, 1915; Fr. Pat. 174,820, Mar. 12, 1915.

SOC. GÉN. DES NITRURES, Ger. Pat. 357,899, Sept. 2, 1922; Br. Pat. 101,091, Mar. 8, 1917.

he gas may be passed through an electrically heated zone before oming in contact with the solid material. In several patents,[1] the itrogen is preheated by passing through the electrodes of a special rc furnace (or through tubes next to the resistance furnace), and then till further heated in the cavity around the electrode before coming n contact with the mixture of alumina and carbon. Serpek[2] preheats he nitrogen to 2000°C. in an electric arc or resistance furnace before ; is passed over a mixture of alumina and carbon in the form of bri- uettes or through a freely falling powdered mixture.

Serpek[3] describes a special process to eliminate the formation of arbides, wherein the powdered alumina and carbon in the presence f nitrogen are fed over and in contact with heated resistance elements hich are kept in motion. This was to be accomplished in a furnace f the rotary type. The mass should not become overheated and arbide is not formed at 1600 to 2000°C., the temperature of the reaction. he resistance elements may be made from suitable proportions of luminum nitride and carbon. Semi-commercial trials of this furnace nowed it to be impractical.

Bunet[4] describes a process in which the mixture of aluminous material nd carbon acts as the heating resistance, the nitrogen coming in contact ith the material as it passes through the furnace. In patents to the ociété Générale des Nitrures,[5] the alumina and carbon are made into riquettes, an excess of carbon being used in order to insure a uniform ow of current through the briquettes, which act as the resistance ement in the furnace. Other good electrical conductors, such as

[1] SERPEK, O., U. S. Pat. 1,060,509, Apr. 29, 1913.

ALUMINIUM INDUSTRIE, A.-G., Fr. Pat. 465,807, Apr. 28, 1914; 1st Add.),975, Dec. 30, 1915; Norw. Pat. 27,191, Aug. 14, 1916; Swiss Pat. 92,977, eb. 1, 1922.

Soc. GÉN. des NITRURES, Fr. Pat. 450,178, Mar. 17, 1913; Ger. Pat. 56,862, Oct. 31, 1913; Br. Pat. 8,347 (1912), Aug. 1, 1912.

[2] SERPEK, O., Fr. Pat. 430,822, Oct. 25, 1911; Br. Pat. 23,541 (1911), eb. 29, 1912.

Soc. GÉN. DES NITRURES, Br. Pat. 11,271 (1915), Dec. 2, 1915; Fr. Pat. 78,886, Jan. 14, 1916.

[3] SERPEK, O., U. S. Pat. 1,030,929, July 2, 1912; Br. Pat. 12,601 (1910), eb. 2, 1911.

[4] BUNET, P., U. S. Pats. 1,145,717; 1,145,748, July 6, 1915; Fr. Pat. 57,723, Sept. 24, 1913; Br. Pat. 24,347 (1913), Apr. 16, 1914.

[5] Soc. GÉN. DES NITRURES, Br. Pats. 10,975 (1913), Nov. 6, 1913; 11,091 913), Feb. 5, 1914; Fr. Pat. 457,650, Sept. 22, 1913; Dutch Pat. 1,279, an. 15, 1917; (C. A. **11**, 1092, 1917).

See also Fr. Pats. 463,390, Feb. 20, 1914; 474,233, Feb. 12, 1915; 510,193, ov. 29, 1920; 436,596, Mar. 30, 1912.

metals, may be substituted for the excess carbon.[1] Shoeld[2] describes a process wherein the alumina and carbon are made into briquettes and are then used as the resistor in an electric furnace. A temperature of 1800 to 2000°C. is required and, in order to utilize the heat, the nitrogen, flowing in a direction opposite to that of the solid material, is preheated by the material which has reacted, while the spent gases preheat the solid material before it enters the reaction zone. In a later patent,[3] Shoeld describes a process which insures a more uniform flow of current and nitrogen through the reacting material. The alumina and carbon are briquetted into the form of cylinders (2 by 1.75 inches) and mixed with irregularly shaped non-fusible carbon resistors 5 to 6 inches in diameter and placed in the electric furnace. After the reaction has taken place, the resistors and the aluminum nitride may be separated by mechanical means. In the process invented by Hoopes[4] and developed by Aluminum Company of America, the mixture of carbon and alumina is made into a self-sustaining porous mass and used as a resistor in an electric furnace. The nitrogen can easily penetrate the porous solid material.

In order to increase the temperature, Coutagne[5] introduces a mixture of combustible gas and oxygen into the chamber in which nitrogen gas and briquettes of alumina and carbon are electrically heated. Hershman[6] heats the charge of aluminous material before it is nitrified, by burning some highly heated gas.

A number of patents covering the design of furnaces for the production of aluminum nitride will not be analyzed, but are listed for purposes of reference.[7]

[1] Soc. Gén. des Nitrures, Br. Pat. 21,366 (1913), Apr. 9, 1911

[2] Shoeld, M., U. S. Pat. 1,274,797, Aug. 6, 1918; Fr. Pat. 497,290, Dec. 2, 1919; Ger. Pat. 349,436, Mar. 2, 1922. Armour Fertilizer Works, Br Pat. 122,829, Apr. 6, 1920.

[3] Shoeld, M., U. S. Pat. 1,344,153, June 22, 1920; Br Pat. 146,919, Jan. 27, 1921; Fr. Pat. 505,793, Aug. 6, 1920; Aus. Pat. 100,687, Aug. 10, 1925. See also U. S. Pats. 1,274,794 to 1,274,798, Aug. 6, 1918.

[4] Hoopes, W., U. S. Pats. 1,393,370; 1,393,371; 1,393,372, Oct. 11, 1921; 1,415,036; 1,415,446, May 9, 1922.

[5] Coutagne, G., Fr. Pat. 472,465, Dec. 8, 1911.
See also U. S. Pat. 1,158,899, Nov. 2, 1915; Fr. Pats. 436,789, Apr. 4, 1912; 469,554, Aug. 4, 1914; 1st Add. 19,926, Nov. 15, 1915; Ger. Pat. 324,867, Sept. 3, 1920; Swiss Pat. 68,989, May 17, 1915; Br. Pat. 12,057 (1914), Dec. 10, 1914.

[6] Hershman, P. R., U. S. Pat. 1,250,874, Dec. 18, 1917.

[7] Aluminium-Industrie A.-G., Swiss Pat. 68,325, Mar. 1, 1915; Norw. Pat. 28,672, Mar. 25, 1918.
Serpek, O., Fr. Pat. 427,066, July 26, 1911; 1st Add. 13,958, Aug. 18, 1911; 2nd Add. 14,338, Aug. 31, 1911; Swiss Pat. 52,902, May 28, 1910;

Special Mixtures.

The patent literature records a wide variety of detail with respect to the composition of the mixture and special conditions to be used in producing aluminum nitride. The suggestions of Sinding-Larsen,[1] Peacock,[2] Bosch and Mittasch,[3] Serpek,[4] and Hershman[5] have had no practical application. The addition of free hydrogen to the nitrogen is said by Serpek[6] to facilitate the reaction. Serpek[7] has also suggested the addition of iron oxide and manganese carbonate as catalysts; Gautrelet[8] uses organic manganese compounds, while De Chalmot,[9] Gerber,[10] and Guilini[11] employ alkaline earth compounds to promote the reaction. Fraenkel and Silbermann[12] have shown that the nature of the

Ger. Pat. 246,334, Apr. 29, 1912; Br. Pats. 29,299 (1910), June 15, 1911; 29,715 (1910), Sept. 7, 1911; 16,522 (1910), Feb. 9, 1911.

DE LOISY, M. C. J. E., U. S. Pat. 1,366,720, Jan. 25, 1921.

EDWIN, E., U. S. Pat. 1,263,389; 1,263,390, Apr. 23, 1918.

ELLIS, C., Br. Pat. 25,630 (1912), May 22, 1913.

HERMAN, E., Ger. Pat. 319,046, Feb. 23, 1920.

LINDBLAD, A. R., U. S. Pat. 1,311,568, July 29, 1919; Norw. Pat. 30,880, July 12, 1920.

SNYDER, F. J., U. S. Pat. 1,305,414, June 3, 1919.

[1] SINDING-LARSEN, A., U. S. Pat. 1,042,723, Oct. 29, 1912.

[2] PEACOCK, S., U. S. Pats. 1,123,585, Jan 5. 1915; 1,154,800, Sept. 28, 1915; 1,134,414, Apr. 6, 1915.

[3] BOSCH, C. and A. MITTASCH, U. S. Pat. 1,054,901, Mar. 4, 1913.

[4] SERPEK, O., U. S. Pat. 1,060,640, May 6, 1913; Br. Pat. 25,141 (1911) Dec. 21, 1911; Fr. Pat. 438,209, May 10, 1912; 1st Add. 15,344, June 18, 1912; Norw. Pat. 23,312, May 13, 1913.

SERPEK, O., U. S. Pat. 1,016,526, Feb. 6, 1912; Br. Pat. 17,611 (1909) July 29, 1910; Fr. Pat. 404,923, Dec. 15, 1909; Ger. Pat. 246,419, May 1, 1912; Can. Pat. 130,031, Dec. 20, 1910; Norw. Pat. 21,712, Oct. 2, 1911; Swed. Pat. 31,997, Dec. 23, 1911; Swiss Pat. 52,901, May 23, 1910.

[5] HERSHMAN, P. R., U. S. Pat. 1,188,651, June 27, 1916.

[6] SERPEK, O., U. S. Pat. 1,078,313, Nov. 11, 1913; Br. Pat. 8,348 (1912) July 25, 1912; Swiss Pat. 60,535, Apr. 4, 1912.

[7] SERPEK, O., U. S. Pat. 1,094,171, Apr. 21, 1914; Br. Pat. 8,349 (1912) Aug. 8, 1912; Fr. Pat. 450,140, Mar. 15, 1913; Swiss Pat. 60,536, Apr. 4, 1912.

DET NORSKE NITRID-AKTIESELSKAB, Norw. Pat. 23,472, June 23, 1913.

[8] GAUTRELET, L. C. E., Fr. Pat. 474,503, Feb. 24, 1915.

[9] DE CHALMOT, G., U. S. Pat. 711,396, Oct. 13, 1903.

[10] GERBER, V., Br. Pat. 199,667, June 28, 1923; Fr. Pat. 559,287, Sept. 2, 1923.

[11] GIULINI, GEBRÜDER, Br. Pat. 22,837 (1913), June 17, 1915; Fr. Pat. 463,232, Feb. 17, 1914; Ger. Pat. 284,531, May 31, 1915; Aus. Pat. 72,238, Aug. 10, 1916.

[12] FRAENKEL, W. and J. SILBERMANN, *Z. Elektrochem.*, **22**, 107–109 (1916); *Chem. Zentr.*, **1**, 1011 (1916).

carbon influences the rate of the reaction, wood charcoal apparently being the best, because of its alkali content.

Bosch and Mittasch[1] add silica, and 5 to 10 per cent of titania or zirconia, with the idea of forming stable nitrides, and lowering the time and temperature of heating necessary to form nitrides, while Peniakoff[2] employs an alkaline earth aluminate heated with carbon to absorb the nitrogen. Still other suggestions include the use of boric anhydride,[3] and Coutagne[4] lists oxygen compounds of silicon, calcium, barium, aluminum, boron, and titanium, as constituents of a suitable mixture for heating with carbon and nitrogen in the preparation of nitrogenous compounds.

Montemartini and Losana[5] have investigated the possibilities of using potassium and aluminum silicates for the fixation of nitrogen or the production of nitrides.

The preparation of an alleged aluminum carbonitride with the formula $Al_2N_2.C_3N_4$ is described in a series of patents by Peacock. A mixture of carbon and nitrogen is heated under reduced pressure (350 to 400 millimeters Hg) at a temperature of 1500°C.[6] If ordinary pressure is used, higher temperatures are required. The aluminum carbonitride is supposed to volatilize and distill during the reaction.

The work of Peacock was repeated by Fraenkel[7] and not the slightest indication was found of the formation of carbonitride at lower pressures, although somewhat greater fixation was obtained at the reduced pressures. The results were very similar to those obtained at atmospheric pressure.

[1] Bosch, C. and A. Mittasch, U. S. Pat. 1,027,312, May 21, 1912; Br. Pat. 16,368 (1910), Feb. 9, 1911; Fr. Pat. 418,425, Dec. 9, 1910; Ger. Pat. 243,839, Feb. 23, 1912; Can. Pat. 135,874, Oct. 3, 1911; Swiss Pat. 52,272, June 25, 1910.

[2] Peniakoff, D. A., U. S. Pat. 1,159,989, Nov. 9, 1915; Fr. Pat. 465,679, Apr. 22, 1914.

[3] Soc. Gén. des Nitrures, Fr. Pat. 437,168, Apr. 15, 1912; Br. Pat 3,344 (1912), May 9, 1912.

[4] Coutagne, G., Fr. Pat. 437,504, Apr. 23, 1912; 1st Add. 15,771, Sept. 19, 1912.

[5] Montemartini, C. and L. Losana, *Giorn. chim. ind. applicata.*, **5**, 487–95 (1923).

[6] Peacock, S., U. S. Pats. 1,031,581, July 2, 1912; 1,035,727, Aug. 13, 1912; 1,129,509, Feb. 23, 1915; 1,143,132, June 15, 1915; 1,134,081, Mar. 30, 1915; 1,129,224, Feb. 23, 1915; 1,137,524, Apr. 27, 1915; 1,154,801, Sept. 28, 1915; Fr. Pat. 448,550, Feb. 3, 1913; Br. Pats. 11,395 (1912), May 13, 1913; 11,390 (1912), May 13, 1913; 11,394 (1912) Feb. 20, 1913; 11,393 (1912) May 13, 1913. *Chem. Eng.*, **18**, 242–5; (C. A. 8, 1062, 1914). See also U. S. Pats. 1,129,506; 1,129,511; 1,129,721, Feb. 23, 1915; 1,134,413, Apr. 6, 1915; 1,031,582, July 2, 1912; Br. Pat. 11,391 (1912), May 13, 1913.

[7] Fraenkel, W., *Z. Elektrochem.*, **19**, 362–373 (1913).

Decomposition and Purification of Aluminum Nitride.

Aluminum nitride might be used directly as fertilizer, but is preferably decomposed to form alumina and ammonia. According to an early patent to Serpek,[1] the aluminum nitride is decomposed by heating with water under pressure at a temperature not exceeding 200°C. Hershman[2] treats the hot aluminum nitride as it comes from the nitrifying chamber with superheated steam at about 600°C. The addition of calcium oxide is said to help the reaction. Later patents to Serpek[3] recommend the use of sodium aluminate lye (20 to 21°Bé.) in which the ratio of soda to alumina is four or five to one. The aluminum nitride is decomposed at boiling temperature with or without pressure. The iron is in the reduced state and does not dissolve, and the silica is also alleged to be insoluble in the weak lye. According to other patents,[4] the aluminum nitride is digested with strong sodium hydroxide to obtain ammonia and alkali aluminate, from which the alumina is obtained by the ordinary Bayer process.

Coutagne[5] states that pulverized aluminum nitride may be decomposed at atmospheric pressure by heating with an alkali or an alkaline earth oxide above 200°C. in the presence of water vapor. Milde[6] uses a mixture of sodium carbonate and calcium hydrate to decompose the aluminum nitride. A stronger alkali aluminate solution is said to be obtained by using this mixture than if the alkali were prepared by a separate reaction.

According to Serpek,[7] metallic iron may be removed from the aluminum nitride by means of dilute acid or chlorine without decomposing

[1] SERPEK, O., U. S. Pat. 884,423, Apr. 18, 1908.

[2] HERSHMAN, P. R., U. S. Pat. 1,261,526, Apr. 2, 1918.

[3] SERPEK, O., U. S. Pats. 1,007,495, Oct. 31, 1911; 13,509 Reissue, Jan. , 1913; 1,040,439, Oct. 8, 1912; Br. Pats. 13,088 (1910), Feb. 2, 1911; 5,997 (1909), Sept. 16, 1909; Fr. Pats. 415,252, Sept. 22, 1910; 454,130, July 4, 1913; Can. Pats. 129,619, Nov. 29, 1910; 145,508, Jan. 28, 1913; *C. A. 7*, 1442, 1913); Norw. Pat. 23,290, May 5, 1913.

[4] SOC. GÉN. DES NITRURES, Ger. Pat. 241,339, Nov. 30, 1911; Norw. Pat. 1,707, Sept. 25, 1911; Swiss Pat. 52,271, May 25, 1910.

SERPEK, O., Fr. Pat. 427,110, July 27, 1911; Swed. Pat. 32,163, Jan. , 1912.

[5] COUTAGNE, G., Fr. Pat. 466,986, May 29, 1914; Ger. Pat. 327,100, Oct. 9, 1920.

[6] MILDE, E., U. S. Pat. 1,115,003, Oct. 27, 1914; Fr. Pat. 459,093, Oct. 5, 1913.

[7] SERPEK, O., U. S. Pat. 1,016,526, Feb. 6, 1912; Br. Pat. 17,611 (1909), July 29, 1910; Fr. Pat. 404,923, Dec. 15, 1909; Ger. Pat. 246,419, May 1, 1912; Can. Pat. 130,031, Dec. 20, 1910; Norw. Pat. 21,712, Oct. 2, 1911; Swed. Pat. 31,997, Dec. 23, 1911; Swiss Pat. 52,901, May 23, 1910.

the nitride. Bosch and Mittasch[1] add limited quantities of acids, bases, or salts, such as aluminum sulfate, to the aluminum nitride, in order to decompose the nitride, but not the impurities present. Temperature and time are important factors in a separation of this nature. In a later patent,[2] they treat the crude mixture with dilute sulfuric acid to destroy sulfides, silicides, and phosphides. Steam passed over the crude nitride for 2 hours, or chlorine for a less time, decomposes sulfides, silicides, phosphides, and carbides (temperature 400 to 600°C.). If desired, the impurities in the nitride may be oxidized by the air at about 700°C. and then leached with dilute sulfuric acid.

According to Palacin,[3] aluminum nitride may be oxidized catalytically to form aluminum nitrate.

If aluminum nitride is heated with hydrogen below 300°C., aluminum hydride (?) and ammonia are said to form.[4] Heating the hydride with nitrogen gas at a temperature above 400°C. gives the original aluminum nitride and more ammonia. According to Kaiser,[5] aluminum nitride reacts with hydrogen sulfide to form aluminum sulfide and ammonia. Nitrogen is supposed to convert the sulfide into aluminum nitride at a temperature of 500 to 700°C., thus completing the cycle. Obviously, there is something wrong with these last three processes, or they would be used for the production of nitric acid and ammonia.

Summary.

The nitride process has everywhere failed to materialize into a successful commercial process, and it may be well to point out some of the difficulties encountered.

In the first place, the temperature required for the nitrification of the carbon and alumina mixture is higher than that claimed in most of the patents and must be controlled within narrow limits. This high temperature promotes the formation of carbides, which cause more trouble than at first anticipated. If overheated, the material fuses together, the porosity, which is so essential for the penetration of the nitrogen gas throughout the mass, is destroyed, and the nitrification ceases before the conversion into nitride is completed. It has been pointed out previously that the furnace linings are quickly destroyed, especially at the higher temperatures. It is also essential that

[1] Bosch, C. and A. Mittasch, U. S. Pat. 1,043,798, Nov. 12, 1912; Br. Pat. 5,382 (1910), Mar. 3, 1911; Ger. Pat. 235,300, June 8, 1911.

[2] Bosch, C. and A. Mittasch, U. S. Pat. 1,102,715, July 7, 1914; Ger. Pat. 237,436, Aug. 19, 1911.

[3] Palacin, N. F. O., Br. Pat. 208,123 (Void) applied for Nov. 6, 1923

[4] Peacock, S., U. S. Pat. 1,521,708, Jan. 6, 1925.

[5] Kaiser, K., Ger. Pat. 346,122, Dec. 24, 1921.

ι reducing atmosphere always be maintained or the carbon nonoxide will burn and the aluminum nitride become oxidized.

While it is fairly easy to decompose amorphous aluminum nitride, the crystalline variety is much more stable. Extensive experiments in the laboratories of Aluminum Company of America have shown that the decomposition of the aluminum nitride by the Bayer process digestion is much slower and more ncomplete than one would be led to believe from the literature. n blowing off the ammonia gas, considerable steam escapes and this loss materially increases the cost of producing alumina. Another very serious problem is the elimination of silica from he aluminate solution, since the ordinary desilication procedures employed in the Bayer process do not satisfactorily precipitate the silica. Why this should be is not definitely known, but at the present time the digestion difficulties alone are sufficient to rule out the nitride process.

✦ SULFIDE PROCESSES

Aluminum sulfide is a yellowish solid which smells rather strongly of hydrogen sulfide on account of its reaction with the moisture of the air. Its heat of formation is considerably below hat of aluminum oxide and, consequently, a number of inventors ave proposed to use it to replace the oxide in the electrolytic ath, expecting a lower power consumption per pound of metal. ts cost, its objectionable and poisonous odor, and the sulfurous ases which would be evolved from the bath, however, make s use for this purpose quite impractical. Its use as a diluent or fused alumina in the Haglund process has already been iscussed (p. 240). Schoenberg[1] uses amounts of sulfide less ıan 3 per cent to increase the fluidity of molten alumina.

The sulfide processes for the production of aluminum or pure lumina are essentially furnace processes. Aluminum sulfide ın be prepared only by a dry method, since in the presence of ater the compound hydrolyzes into hydrated alumina and ydrogen sulfide. Aluminum sulfide might be reduced to uminum by electrolyzing in a fused sulfide bath, or may be rst converted into alumina which is then used in the regular yolite bath.

Various processes have been suggested for the production of anhydrous uminum sulfide. The first to be considered will be those which use

[1] Schoenberg, G. (Metallbank), Br. Pat. 279,870, Mar. 1, 1928.

carbon disulfide, carbon oxysulfide, or sulfur vapor as sulfidizing agents. Jaennigen[1] heats a mixture of alumina and sodium carbonate with carbon disulfide and then electrolyzes the fused bath in an atmosphere of carbon disulfide. Peniakoff[2] heats anhydrous aluminum sulfate with carbon disulfide to a dull red heat and obtains aluminum sulfide, elementary sulfur, and carbon dioxide. Double sulfides of aluminum[3] are prepared by heating anhydrous alumina with oxysalts of metals, such as sulfates, phosphates, etc., together with carbon disulfide or carbon oxysulfide. The metallic aluminates also may be converted into double sulfides by heating with carbon disulfide, carbon oxysulfide, or sulfur vapor.[4] It is stated that this reaction is exothermic in nature.[5] Blackmore[6] proposes to dissolve alumina in a molten electrolyte consisting of 2 parts cryolite and 1 part potassium fluoride and then pass carbon disulfide through the molten mass to form aluminum sulfide. He also states that an electrolyte consisting of cryolite and a mixture of potassium and sodium chlorides melts at a lower temperature than the ordinary electrolyte. Alumina dissolved in this electrolyte reacts with carbon disulfide to form aluminum sulfide which dissolves, avoiding the formation of a crust or film.[7] According to foreign patents,[8] feldspar and similar substances are treated with sulfur vapor to form a mixture of potassium and aluminum sulfides, which react with the silica to form oxysulfosilicates, or at a higher temperature, sulfosilicates, which can be decomposed with acids or water under pressure.

Aluminum sulfide or double sulfides of aluminum and another metal may be prepared by fusing aluminum compounds with a metallic sulfide. According to Peniakoff,[9] a mixture of aluminum sulfate, metallic sulfide, and sulfur is heated to form a double sulfide. The sulfur vapor stops the formation of metallic sulfate by combining with the oxygen. Alum may be heated with sulfur to form a double sulfide. Keogh and Douglas[10] add a mixture of aluminum sulfate and carbon to a fused bath of sodium chloride. The sodium chloride acts as a

[1] JAENNIGEN, Fr. Pat. 242,729, applied for Nov. 9, 1894; Swiss Pat. 8,256 Feb. 5, 1894.

[2] PENIAKOFF, D. A., U. S. Pat. 606,576, June 28, 1898; Ger. Pat. 79,781, Feb. 6, 1895.

[3] PENIAKOFF, D. A., Br. Pat. 7,273 (1896), July 25, 1896; Ger. Pats. 87,898, July 7, 1896; 88,840, Sept. 23, 1896.

[4] BLACKMORE, H. S., U. S. Pat. 605,458, June 7, 1898.

[5] PENIAKOFF, D. A., Fr. Pat. 661,675, applied for Oct. 22, 1895; Ger. Pat. 94,845, Oct. 30, 1897; Br. Pat. 6,290 (1896), June 20, 1896.

[6] BLACKMORE, H. S., U. S. Pat. 605,812, June 14, 1898.

[7] BLACKMORE, H. S., U. S. Pat. 605,378, June 7, 1898.

[8] NORSK HYDRO-ELEK. KVAEL., Fr. Pat. 498,888 Jan. 24, 1920; Norw. Pat. 32,205, Apr. 25, 1921.

[9] PENIAKOFF, D. A., Ger. Pat. 86,523, Apr. 13, 1896.

[10] KEOGH, L. R. and C. A. DOUGLAS, Br. Pat. 18,356 (1908), Sept. 1, 1909.

used solvent for the aluminum sulfate and carbon. Double sulfides are prepared by adding a mixture of two sulfates and carbon to the used bath. Peniakoff[1] states that aluminum sulfide is formed by the double decomposition taking place between anhydrous aluminum salts and the sulfides of the alkalies or alkaline earth in a suitable flux. The aluminum sulfide, according to Peniakoff, can be reduced directly in the molten bath by the electric current or by means of reducing gases such as the hydrocarbons! Alkali ores are heated with ferro-silicon and pyrites with the formation of an alkali aluminous slag containing sulfides.[2] Bergve[3] heats alkali aluminum silicate with sulfur at 800 to 1400°C. to form sulfosilicates which can be readily decomposed with water at high temperatures or with weak acids. For the preparation of metallic aluminum or iron-free aluminum compounds, Goldschmidt and Ravner[4] fuse plagioclase rocks of the labradorite-anorthite series with alkali or alkaline earth sulfides, and sulfur or carbon, obtaining thereby aluminum sulfide which floats to the top of the bath. Whittington[5] heats dry aluminum chloride with calcium sulfide at 60 to 80°C. and obtains a mixture of aluminum sulfide and calcium chloride which is separated by means of alcohol.

When alumina or aluminous ore is mixed with carbon and a metal sulfide and heated to a high temperature, part of the alumina is reduced to metallic aluminum, resulting in the formation of an aluminum alloy and a sulfidic slag containing aluminum sulfide.[6]

Iron sulfide (pyrites) has been used in several commercial processes to convert crude aluminum alloys or aluminum compounds into aluminum sulfide. While other heavy metal sulfides can be used and are mentioned in the patent literature, pyrites is the cheapest and most practical.

In the patent to Skappel,[7] aluminum sulfide is prepared by heating an aluminum-iron alloy with a heavy metal sulfide, such as iron sulfide. The resulting aluminum sulfide floats on top and can be tapped off and used for the preparation of alumina or aluminum. Any silicon present remains with the iron in the form of ferrosilicon. Vautin[8]

[1] PENIAKOFF, D. A., Br. Pat. 11,555 (1896), Apr. 3, 1897; Ger. Pat. 9,143, Oct. 10, 1896; Norw. Pat. 5108, June 2, 1896; Swed. Pat. 8045, July 0, 1897.

[2] NORSK HYDRO-ELEK. KVAEL., Fr. Pat. 500,814, Mar. 25, 1920.

[3] BERGVE, E., U. S. Pat. 1,346,365, July 13, 1920.

[4] GOLDSCHMIDT, V. M. and O. RAVNER, Norw. Pat. 29,440, Feb. 10, 1919.

[5] WHITTINGTON, J. A., U. S. Pat. 1,549,398, Aug. 11, 1925.

[6] HAGLUND, T. R., Swed. Pat. 57,495, Sept. 16, 1924; U. S. Pat. 1,512,462, Oct. 21, 1925.

ONDA, M., U. S. Pat. 760,554, May 24, 1904.

[7] SKAPPEL, H., Norw. Pat. 44,467, Oct. 10, 1927.

[8] VAUTIN, C. T. J., U. S. Pat. 513,660, Jan. 30, 1894; Ger. Pat. 75,825, June 11, 1894.

has patented a process for the production of aluminum sulfide which consists in heating lead sulfide with metallic aluminum at 900 to 1000°C.

Haglund, Magnusson, and Lundin[1] fuse a mixture of alumina, aluminum carbide, carbon, and iron sulfide and obtain aluminum sulfide and iron. The process also can be applied to silicates or impure bauxites. The heavy metal impurities and the silica are reduced by carbon and alloy with the iron. Halvorsen[2] fuses clay with a mixture of iron sulfide and carbon in the electric furnace and obtains ferrosilicon and aluminum sulfide. Haglund[3] fuses clay or other similar aluminous material in an electric arc furnace, together with a reducing agent and one or more sulfur compounds, such as iron sulfide. The composition of the charge is so adjusted that there is also some metallic aluminum in the iron alloy. In order to stabilize the aluminum sulfide to the action of air, another sulfide, such as sodium or calcium sulfide, may be added before the fused mass is tapped.

In the description of the Haglund process (see p. 241) several methods for the decomposition of aluminum sulfide were mentioned. A recent patent[4] claims that the reaction between aluminum sulfide (or a mixture of alumina and aluminum sulfide) and calcium oxide is quite vigorous when once started. The calcium sulfide is dissolved by means of water and dilute acid, while the alumina is only slightly soluble, since it has been heated to such a high temperature.

In the patent to Condy,[5] bauxite is fused with an alkali or alkaline earth sulfide, forming a sulfoaluminate. This compound is extracted with water and treated with a weak acid, such as carbonic or acetic. Several similar patents have been considered under the aluminate processes.

x ALUMINUM CARBIDE IN THE PRODUCTION OF ALUMINA

Aluminum carbide seems to exist in two forms. The common one, formed at high temperatures but below its melting point, is a mass of yellow, flake-like crystals, very slowly decomposed by water or acids, evolving methane.[6] At very high temperatures there is formed a black fused mass which is even more stable chemically. Various processes for the preparation of alumina

[1] HAGLUND, T. R., O. O. MAGNUSSON, and H. LUNDIN, Swed. Pat. 53,911, Mar. 7, 1923.

[2] HALVORSEN, B. F., Norw. Pat. 21,010, Jan. 9, 1911.

[3] HAGLUND, T. R., Norw. Pat. 38,590, Dec. 17, 1923; Swed. Pat. 54,107, Mar. 28, 1923.

[4] METALLBANK U. METALLURGISCHE Ges., A.-G., and CONWAY, BARON VON GIRSEWALD, Br. Pat. 294,079, July 19, 1928; Fr. Pat. 650,193, Jan. 5, 1929.

[5] CONDY, H. C., Br. Pat. 4618 (1877), June 6, 1878.

[6] MOISSAN, Compt. rend., 119, 16 (1891). See also MATIGNON, C., Chem. Ztg., 32, 53 (1908); Ann. chim. phys., (8) 13, 276 (1908).

ave been described in which the aluminous material is first
onverted into aluminum carbide; this compound is decomposed
a later step to give alumina. The preparation of alumina
y this method has only very limited possibilities. Although
he insoluble aluminous materials may be converted into alu-
inum carbide, and some of the impurities volatilized at the
xtremely high temperatures necessary for the reaction, other
ethods accomplish the same results at less expense.

Barnett and Burgess[1] produce aluminum carbide by heating bauxite,
e., with an excess of carbon to a temperature of about 2000°C. A
ecial electric furnace is used in which a small portion of the charge
heated until the reaction is complete and then a fresh portion is
ated. Durville[2] prepares aluminum carbide which is then heated in
ygen to form molten alumina.

According to Weber,[3] kaolin is smelted in an electric furnace with
ke to produce a mixture of aluminum carbide and silicon carbide.
he mixture is decomposed with water to form methane, aluminum
rdrate, and unchanged silicon carbide. The aluminum hydrate is
ashed out from the heavier silicon carbide and calcined. Peacock[4]
ats a mixture of potassium aluminum silicate and finely ground
rbon to 1200 to 1400°C., while reducing below the normal the partial
essures of the reaction products. The main products of the reaction
e said to be silica, potassium carbide, and aluminum carbide. The
rbides are decomposed in an autoclave with superheated steam,
burned in air to form potassium carbonate and alumina. Valatelli
d Vialars[5] prepare aluminum carbide by heating a mixture of bauxite
clay, iron, and carbon in the electric furnace. The carbide is con-
rted into alumina by heating with steam under pressure in an
toclave.

According to a British patent,[6] clay and coke are heated in the
ctric furnace to form chiefly carbides of silicon and aluminum.
ustic soda reacts with the aluminum carbide to form soluble sodium
minate and methane, but does not dissolve the silicon, titanium,
d iron carbides. Hershman[7] prepares a mixture of alumina and
minum carbide by heating calcined alunite (from which the potash

Barnett, M. and L. Burgess, U. S. Pats. 1,222,593, Apr. 17, 1917;
19,797, Mar. 20, 1917; Br. Pat. 112,929, Jan. 27, 1919; Fr. Pat. 488,203,
t. 14, 1918.

Durville, P. H. G., Ger. Pat. 323,523, July 27, 1920.

Weber, F. C., U. S. Pat. 728,528, May 19, 1903.

Peacock, S., U. S. Pat. 1,129,505, Feb. 23, 1915.

Valatelli, G. and R. Vialars, Fr. Pat. 513,525, Feb. 17, 1921.

General Electric Co., Br. Pat. 3998 (1904), Dec. 31, 1904.

Hershman, P. R., U. S. Pat. 1,137,617, Apr. 27, 1915.

has been removed) with carbon to a temperature of about 1650°C. in an atmosphere of carbon monoxide. It is stated that nearly all of the alumina is thus rendered soluble in alkali. Patrouilleau[1] states that aluminum carbide is decomposed by a cold alkali solution, but by heating the mixture the reaction is completed in a shorter period of time. The alumina is precipitated from the alkali aluminate and the solution used to decompose more carbide.

X   ALUMINUM CHLORIDE

Aluminum chloride exists in both hydrated and anhydrous forms. The hydrated forms can be obtained only by crystallization from aqueous solutions, and on heating they decompose into alumina, water, and hydrochloric acid. The anhydrous chloride can be prepared only in the dry way. It was first made by Oersted in 1825 by passing chlorine gas over a heated mixture of alumina and carbon. Oersted subsequently prepared metallic aluminum from the chloride by reduction with potassium amalgam. Aluminum chloride is a yellowish-white, deliquescent solid, which fumes in moist air. Aluminum chloride reacts readily with moisture with the formation of alumina and hydrochloric acid. The pure chloride sublimes readily at the relatively low temperature of about 180 to 195°C. It forms double salts with the alkali chlorides, and with phosgene. It is reported that all anhydrous aluminum chloride made from the reaction of chlorine on alumina and carbon contains phosgene, consequently for organic syntheses the compound should be made from metallic aluminum and chlorine or hydrochloric acid.

Aluminum chloride in the form of the double compound with sodium chloride ($NaCl.AlCl_3$) was early used in the commercial production of aluminum by the sodium reduction process. Attempts were also made to develop an electrolytic reduction process, using a fused electrolyte of the double chloride of aluminum and sodium. This compound melts at about 185°C., and mixtures of sodium chlorides and aluminum chloride in other proportions are completely fluid at substantially lower temperatures. Aluminum oxide is not appreciably soluble in the electrolyte, however, and for other reasons outlined in Chap. I the process was unsuccessful.

Aluminum chloride has, however, other very valuable applications in industry. Perhaps the most important of these is its use in the oil industry as a cracking agent. McAfee and other

[1] Patrouilleau, L. G., Fr. Pat. 475,455, May 18, 1915.

ɔrkers of the Gulf Refining Company have been very active
the commercial development of cracking processes employing
ɹminum chloride. A considerable tonnage of aluminum
loride is also consumed by the dyestuff industry, as it is an
tive condensation agent in many chemical reactions.   Another
ɪportant use of aluminum chloride is in the carbonizing of wool.
ɹlston has prepared an excellent summary of the processes of
aking aluminum chloride.[1]

Some of the simplest methods for the preparation of aluminum
loride are based on the reaction of chlorine with metallic
ɹminum.   The reaction is exothermic and if pure chlorine
ɪd aluminum are used, there are no impurities to contaminate
ɛ product.   The cost of metallic aluminum, however, limits
ɛ application of this method.   The reaction of chlorine with
ɹminum at ordinary temperatures is slow, but proceeds
gorously if the aluminum is heated.   The formation of oxide
ɪns on the aluminum hinders the reaction, but the formation
  aluminum chloride is rapid and continuous if chlorine is
ɪbbled through the molten aluminum, as in the process of
·ooks.[2]

Frary[3] has devised a method which utilizes aluminum dross
ɪstead of virgin aluminum.   This dross contains both aluminum
ɛtal and aluminum oxide.   If carbon is added to the dross
ɪd chlorine passed through the mixture, the heat of reaction
tween the metallic aluminum and chlorine is sufficient to
ɪmplete the reaction between alumina, carbon and chlorine,
  that both the metallic aluminum and the aluminum oxide
ɛ converted to chloride.   Other variations on the process
· those of Gibbs,[4] who treats aluminum with liquid chlorine,
ɪd Jacobson,[5] who uses bromine with the chlorine to facilitate
ɪction; of Thofehrn,[6] who atomizes molten aluminum in the

RALSTON, O. C., *Bur. Mines Tech. Paper* **321**, 38 pp. (1923).
: BROOKS, B. T., U. S. Pat. 1,165,065, Dec. 21, 1915.
³ FRARY, F. C., U. S. Pat. 1,351,818, Oct. 5, 1920; Br. Pat. 163,975,
ɪe 30, 1922; Fr. Pat. 534,839, Apr. 3, 1922; Ger. Pat. 397,673, June 27,
24; Norw. Pat. 33,718, Jan. 2, 1922; Swed. Pat. 53,023, Nov. 15, 1922;
iss Pat. 97,867, Feb. 16, 1923.
  See also McAFEE, A. M., U. S. Pat. 1,544,328, June 30, 1925.
  SHOELD, M., U. S. Pat. 1,375,116, Apr. 19, 1921.
· GIBBS, H. D., U. S. Pat. 1,422,560, July 11, 1922.
' JACOBSON, B. H., U. S. Pats. 1,445,082, Feb. 13, 1923; 1,474,479, Nov.
1923; Br. Pat. 190,688, Dec. 28, 1922; Ger. Pat. 378,372, July 12, 1923.
³ THOFEHRN, H., Ger. Pat. 83,267, Oct. 17, 1895.

presence of chlorine, as well as proposals by Kirkpatrick and
Morgan,[1] Pelzer and Herthel.[2] Other inventors as Askenasy,[3]
Burgess,[4] and Mabery[5] have used hydrochloric acid instead
of chlorine with aluminum and aluminum alloys in the production
of aluminum chloride. Patrouilleau[6] proposes to make an
aluminum-silicon alloy in the electric furnace and then treat
it with chlorine.

Aluminum Chloride from the Oxide with Carbon and Chlorine

For the large-scale production of aluminum chloride for use
in oil-cracking processes, it seems more feasible to use bauxite
as the source of the aluminum, and carbon and chlorine as the
reagents. McAfee[7] has described a plant operating along these
lines. The principal difficulties in the commercialization of this
reaction are in securing efficient utilization of the materials and
the provision of suitable apparatus for the carrying out of the
reaction. An intimate mixture of the reacting materials is
necessary for efficient conversion of the oxide to chloride.
McAfee,[8] for example, prepares briquettes of bauxite and coking
coal and, after calcining, heats them at 1600 to 1800°F. in a
stream of chlorine gas. The iron and titanium chlorides are
not removed, as these compounds do not interfere with the
cracking of oils. Heating the briquettes at 100 to 200°C. is
said to be sufficient, since the heat of reaction raises the tempera-
ture.[9] In the process of King and Roberts,[10] a finely ground or
granular mixture of alumina and carbon is preheated to the
necessary temperature and the chlorine allowed to react with the
mixture while it is blown through the chamber by the large
volume of chlorine gas necessary for the reaction.

[1] KIRKPATRICK, B. S. and F. S. MORGAN, U. S. Pat. 1,455,005, May 15,
1923.

[2] PELZER, H. L. and E. C. HERTHEL, U. S. Pat. 1,541,068, June 9, 1925.

[3] ASKENASY, P., Ger. Pat. 76,909, applied for Feb. 6, 1891.

[4] BURGESS, L., U. S. Pat. 1,566,269, Dec. 22, 1925.

[5] MABERY, C. F., U. S. Pat. 351,184, Oct. 19, 1886.

[6] PATROUILLEAU, L. G., Fr. Pat. 481,106, Oct. 31, 1916.

[7] McAFEE, A. M., *J. Ind. Eng. Chem.*, **21**, 670 (1929).

[8] McAFEE, A. M., U. S. Pats. 1,217,171, Feb. 27, 1917; 1,513,931, June
30, 1925.

[9] I. G. FARBENINDUSTRIE, A.-G., Br. Pat. 275,915, Jan. 5, 1928.

[10] KING, G. H. and G. I. ROBERTS, U. S. Pat. 1,268,015, May 28, 1918.

In treating double silicates such as feldspar, a large amount chlorine is used up in forming silicon tetrachloride, which s little value. The chlorides of aluminum and potassium n be formed without the formation of silicon tetrachloride treating feldspar with one-fourth the usual amount of chlorine d carbon.[1]

McAfee[2] claims that the reaction between alumina, carbon, d chlorine is accelerated by the presence of a certain amount returned waste gases coming from the reaction itself. The dition of sulfur chloride is also said to make the reaction take ice at a lower temperature.[3]

Alumina can be chlorinated with phosgene or a mixture of rbon monoxide and chlorine.[4] According to a German tent,[5] carbon monoxide and chlorine are passed over heated .y or bauxite. The iron oxide is reduced by the carbon moxide and then converted into the volatile chloride by the orine. By carrying the reaction farther, volatile aluminum oride is formed. In place of the carbon monoxide and orine, a mixture of sodium chloride and carbon can be used. preliminary treatment of alumina with a mixture of carbon moxide and chlorine (or phosgene) is said to remove the orides of iron and titanium, since they form more rapidly .n aluminum chloride.[6] To form the aluminum chloride, s only necessary to heat the purified alumina to about 450°C. an insulated furnace with the carbon monoxide and chlorine, er which the heat of reaction supplies sufficient heat. King l Roberts[7] pass a mixture of carbon monoxide (producer gas) l chlorine over heated alumina, preferably with added carbon l in the form of briquettes. Heap and Newberry[8] pass a

SIEMENS and HALSKE, A.-G., Ger. Pat. 289,909, Jan. 25, 1916.

McAFEE, A. M., U. S. Pat. 1,578,052, Mar. 23, 1926.

CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE, Br. Pat. 176,811 id), applied for Mar. 13, 1922; Fr. Pat. 548,691, Jan. 20, 1923.

BUDNIKOV, P. P., Z. angew. Chem., **37**, 100–101 (1924).

BERGIUS, H. AND Co., Ger. Pat. 10,393, Aug. 15, 1887.

I. G. FARBENINDUSTRIE, A.-G., Fr. Pat. 645,335, Oct. 23, 1928. See DEARBORN, R. J., Can. Pat. 283,609, Sept. 25, 1928.

KING, G. H. and G. I. ROBERTS, U. S. Pat. 1,308,080, July 1, 1919. also I. G. FARBENINDUSTRIE, A.-G., Br. Pat. 281,191, Dec. 8, 1927.

HEAP, W. and E. NEWBERRY, U. S. Pat. 1,331,257, Feb. 17, 1920; Br. ;. 130,626, Aug. 14, 1919; 131,039, Aug. 21, 1919; Fr. Pat. 496,258 31, 1919; Norw. Pat. 33,717, Jan. 2, 1922.

mixture of producer gas and chlorine or phosgene over alumina or an aluminum salt of a weak acid, and obtain aluminum chloride.

A recent German patent[1] describes a process in which alumina and carbon are heated with a mixture of hydrogen and chlorine (in excess). The heat of reaction between the hydrogen and chlorine is said to elevate the temperature sufficiently to distill the aluminum chloride formed by the excess chlorine.

Reducing agents other than carbon or carbon monoxide have been suggested for the production of aluminum chloride from alumina. Stafford, Gardner, and Phillips[2] heat alumina or an aluminum silicate low in iron to a dull red heat in the electric furnace until the water is eliminated and then treat the material with a mixture of chlorine and sulfur subchloride. Hall[3] conducts gaseous sulfur and chlorine either over heated alumina or through a molten bath in which the alumina is dissolved, and obtains aluminum chloride. It is stated that the reaction is highly exothermic.

According to Mardick,[4] 1 part of calcium oxide and 4 parts of water-free alumina are treated with a mixture of carbon disulfide and chlorine at 700 to 1200°C. under pressure. Calcium sulfate remains as a residue and the aluminum chloride treated with vapors of carbon tetrachloride or petroleum in the condenser is less hygroscopic than the usual product.

Other proposals have been made by Prichard and Henderson,[5] McKee,[6] Goldschmidt and Ravner,[7] Weaver,[8] Hall,[9] Wohlers,[10]

[1] VEREIN FÜR CHEMISCHE UND METALLURGISCHE PRODUKTION in AUSSIG, Ger. Pat. 455,266, Jan. 28, 1928.

[2] STAFFORD, J. G., R. H. GARDNER, and E. B. PHILLIPS, U. S. Pat. 1,489,021, Apr. 1, 1924. See also SINDING-LARSEN, A., Norw. Pat. 39,911, Oct. 13, 1924.

[3] HALL, F. W., U. S. Pats. 1,405,115, Jan. 31, 1922; 1,422,565, July 11, 1922.

[4] MARDICK, J. R., U. S. Pat. 1,325,203, Dec. 16, 1919.

[5] PRICHARD, G. L. and H. HENDERSON, U. S. Pat. 1,616,549, Feb. 8, 1927.

[6] McKEE, R. H., U. S. Pat. 1,509,605, Sept. 23, 1924.

[7] GOLDSCHMIDT, V. M. and O. RAVNER, U. S. Pat. 1,302,852, May 6, 1919; Br. Pat. 113,278, Jan. 23, 1919; Norw. Pat. 30,823, June 21, 1920.

[8] WEAVER, V. M., U. S. Pats. 1,511,646, Oct. 14, 1924; 1,241,796, Oct. 2, 1917; 1,300,205, Apr. 8, 1919; 1,238,604, Aug. 28, 1917; Br. Pat. 103,716, Feb. 8, 1917; Fr. Pat. 481,056, Oct. 27, 1916.

[9] HALL, F. W., U. S. Pats. 1,468,632, Sept. 25, 1923; 1,503,648, Aug. 5, 1924; 1,549,766, Aug. 18, 1925; 1,619,022, Mar. 1, 1927.

[10] WOHLERS, F. T., U. S. Pat. 1,564,302, Dec. 8, 1925.

ontgelas,[1] van der Leeden,[2] Faure,[3] Foote[4], Simon and Per-
)t,[5] von Kügelgen,[6] Schröder,[7] Dearborn,[8] and Wolcott.[9]

·ocesses Using Chlorides as Source of Chlorine.

Alkali or alkaline earth chlorides have been proposed as a cheap
urce of chlorine for the production of aluminum chloride or the double
lorides. Booth and Marshall,[10] for example, heat a mixture of alumin-
s material, silica, calcium chloride, and carbon in the electric furnace
a temperature of about 1200°C. The iron chloride is volatilized
)ng with the aluminum chloride, but since the former condenses at
0°C. and the latter at 183°C., the mixture is easily separated by
.ctional condensation. The silica unites with the calcium to form
lcium silicate. Another process using calcium chloride is that of
ardick,[11] who heats a mixture of calcined bauxite, calcium chloride,
d carbon at 700 to 800°C. in an electric furnace. The temperature
raised progressively to 2000°C., resulting in the formation of calcium
·bide and volatile aluminum chloride.

5odium chloride, while cheap, has the disadvantage of tending to
latilize with the aluminum chloride at elevated temperatures. The
ll-known process of Deville was early used to prepare the double
oride by passing chlorine gas over highly heated alumina, carbon,
l salt. Processes using sodium chloride have been patented by
acock,[12] Raynaud,[13] Frishmuth,[14] Dutt and Dutt,[15] and Schroeder.[16]

[1] DE MONTGELAS, COUNT R., Br. Pats. 10,011 (1886) applied for Aug. 4,
36; 10,013 (1886), applied for Aug. 4, 1886.

[2] VAN DER LEEDEN, R., Fr. Pat. 466,721, May 22, 1914; Ger. pat.
;,867, Dec. 5, 1913.

[3] FAURE, C. A., Ger. Pat. 62,907, June 16, 1892.

[4] FOOTE, E., Br. Pat. 1995 (1883), applied for Oct. 18, 1883.

[5] SIMON, A. and L. PERNOT, Fr. Pat. 406,590, Feb. 2, 1910.

[6] VON KÜGELGEN, F., U. S. Pat. 1,147,832, July 27, 1914.

[7] SCHRÖDER, H., U. S. Pat. 991,096, May 2, 1911; Austrian Pat. 34,350,
)t. 10, 1908.

[8] DEARBORN, R. J., U. S. Pats. 1,600,216, Sept. 21, 1926; 1,605,098,
v. 2, 1926.

[9] WOLCOTT, E. R., U. S. Pats. 1,506,104, Aug. 26, 1924; 1,528,039, Mar.
925; 1,633,835, June 28, 1927; 1,612,686, Dec. 28, 1926; Br. Pat. 175,006,
). 1, 1922; Fr. Pat. 527,068, Oct. 20, 1921.

BOOTH, H. S. and G. G. MARSHALL, U. S. Pats. 1,392,043; 1,392,044,
t. 27, 1921.

MARDICK, J. R., U. S. Pat. 1,600,899, Sept. 21, 1926.

PEACOCK, S., U. S. Pat. 1,507,709, Sept. 9, 1924.

PARSONS, C. E. and S. PEACOCK, U. S. Pats. 1,525,041; 1,525,042, Feb.
925.

RAYNAUD, F., U. S. Pat. 599,111, Feb. 15, 1898; Br. Pat. 12,266 (1897)
/ 24, 1897; Ger. Pat. 97,010, Mar. 16, 1898; Dan. Pat. 1426, Jan. 19,
8; Norw. Pat. 5906, Dec. 20, 1897; Swed. Pat. 8474, Nov. 20, 1897.

Taddei[1] obtains the chlorine by electrolyzing fused sodium chloride at 1000°C. and conducts it over a mixture of dehydrated alumina and liquid tar at a temperature of 1300 to 1500°C.

Danckwardt[2] places a mixture of alumina and carbon in contact with the positive pole in a fused bath of zinc chloride and then collects the anhydrous aluminum chloride which volatilizes.

Aluminum Chloride from the Carbide, Nitride, Sulfide, Etc.

In place of alumina or other natural aluminous ores, compounds of aluminum, such as the carbide, nitride, sulfide, sulfate, etc., may be used to produce aluminum chloride. Smith and Essex[3] prepare aluminum chloride by heating crude aluminum carbide with chlorine or hydrochloric acid. After the charge reaches a temperature of 200°C., the reaction with chlorine goes on without further heating, and it is stated that since iron is not attacked at this temperature by dry chlorine, an iron container can be used.

In a patent to Burgess,[4] a process is outlined in which finely divided aluminum carbide is suspended in hydrochloric acid gas and external heat applied to initiate the exothermic reaction which produces anhydrous aluminum chloride. Barnett and Burgess[5] treat a mixture of aluminum carbide and metallic aluminum with dry hydrochloric acid gas at a temperature of 600 to 900°C. and obtain volatile aluminum chloride which condenses at a lower temperature. In another patent to Burgess,[6] aluminum carbide is heated in a furnace with a chloride such as lead chloride. The aluminum chloride volatilizes, leaving behind a residue consisting of lead and carbon.

Haglund[7] first prepares aluminum sulfide by fusing alumina or clay with a reducing agent and a sulfide, such as iron sulfide.

[1] TADDEI, G., Br. Pat. 13,379 (1901).

[2] DANCKWARDT, P., U. S. Pat. 1,343,662, June 15, 1920; Br. Pat. 168,643, Sept. 2, 1921; Fr. Pat. 517,049, Apr. 29, 1921; Ger. Pat. 380,502, Sept. 10, 1923.

[3] SMITH, D. F. and H. ESSEX, U. S. Pat. 1,270,226, June 18, 1918.

[4] BURGESS, L., U. S. Pat. 1,105,183, Jan. 31, 1922.

[5] BARNETT, M. and L. BURGESS, U. S. Pat. 1,218,588, Mar. 6, 1917; Br. Pat. 109,790, Feb. 14, 1918; Fr. Pat. 486,801, May 14, 1918; Ger. Pat. 325,474, Sept 13, 1920; Norw. Pat. 29,985, Sept. 1, 1919; Dan. Pat. 23,219, June 22, 1918; Neth. Pat. 4,983, June 1, 1920.

[6] BURGESS, L., U. S. Pat. 1,321,281, Nov. 11, 1919.

[7] HAGLUND, T. R., Fr. Pat. 596,293, Oct. 20, 1925; Swed. Pat. 60,424, Mar. 23, 1926; Swiss Pat. 120,514, June 1, 1927; Norw. Pat. 44,326, Aug. 22, 1927.

[14] FRISHMUTH, W., U. S. Pat. 359,601, Mar. 22, 1887; Br. Pat. 10,011 (1886) applied for Aug. 4, 1886.

[15] DUTT, E. E. and P. C. DUTT, Br. Pat. 123,213, Feb. 20, 1919.

[16] SCHROEDER, H., Norw. Pat. 17,645, applied for Oct. 31, 1907.

he aluminum sulfide is then treated with chlorine or chlorine com-
ounds to form anhydrous aluminum chloride which is volatile at a
mperature slightly higher than that of the reaction.   Free chlorine
sulfur may be removed from the aluminum chloride by heating with
uminum sulfide or calcium carbide.

Baum and Jones[1] propose to make aluminum chloride by heating
iquettes of aluminum nitride containing 4 to 5 per cent carbon and a
all amount of alumina with chlorine gas at a temperature of 600 to
0°C.   Miner[2] treats a mixture of aluminum nitride and carbonaceous
aterial with hydrogen chloride at a temperature of 900 to 1500°C.
uminum chloride and valuable nitrogen compounds are obtained.

According to Vaughan,[3] alumina is heated to redness and subjected
the vapors of carbon disulfide and dry hydrochloric acid gas.   The
lfides formed by the carbon disulfide are converted into volatile
lorides by the action of the hydrochloric acid gas.   The aluminum
loride is separated from the volatile chlorides of the impurities
 fractional distillation.

Processes using aluminum sulfate have been patented by Blumen-
rg,[4] Humphrey,[5] Lea and Humphrey,[6] White,[7] and Tilley.[8]

urification of Aluminum Chloride.

In the preparation of pure aluminum chloride, the chlorides of silicon
d titanium are readily separated because of their greater volatility.
rric chloride, although less volatile than aluminum chloride, cannot
satisfactorily separated from it by fractional condensation or sublima-
n.   Ferrous chloride is less volatile than ferric chloride, and Deville
de use of this fact in purifying aluminum chloride.   Castner claimed
at iron could be removed by melting aluminum chloride under pressure
d electrolyzing,[9] or by adding finely divided aluminum to precipitate
e iron;[10] other processes using metallic aluminum have been proposed

[1] BAUM, E. C. and D. O. JONES, U. S. Pat. 1,372,332, Mar. 22, 1921;
rw. Pat. 33,719, Jan. 2, 1922.

[2] MINER, C. G., U. S. Pat. 1,688,504, Oct. 23, 1928.

[3] VAUGHAN, E. P. H., Br. Pat. 1630 (1868), applied for Nov. 19, 1868.

[4] BLUMENBERG, H., U. S. Pat. 1,649,383, Nov. 15, 1927.

[5] HUMPHREY, C. W., U. S. Pat. 1,546,290, July 14, 1925.

[6] LEA, H. I. and C. W. HUMPHREY, U. S. Pats. 1,546,289, July 14, 1925;
558,897, Oct. 27, 1925; 1,646,732 and 1,646,733, Oct. 25, 1927.

[7] WHITE, W., Br. Pat. 12,543 (1888), June 29, 1889.

[8] TILLEY, G. S., U. S. Pat. 1,661,100, Feb. 28, 1928.

[9] CASTNER, H. Y., U. S. Pat. 422,500, Mar. 4, 1890; Br. Pat. 18,062
889), Sept. 13, 1890; Ger. Pat. 54,877, Jan. 5, 1881; Swiss Pat. 1911, Feb.
1890.

[10] CASTNER, H. Y., U. S. Pat. 409,668, Aug. 27, 1889; Br. Pat. 1989 (1889),
e. 7, 1889; Ger. Pat. 52,770, July 16, 1890.

by Weaver,[1] Pollak,[2] Humphrey and McKittrick.[3] Prichard and Henderson[4] also propose to remove silicon tetrachloride by reaction with aluminum.

The vapors of aluminum chloride may be continuously removed from the reaction chamber and dissolved in a protective liquid, such as a hydrocarbon oil. Certain impurities are removed by this procedure and the aluminum chloride is kept in an anhydrous state.[5]

Ethyl and methyl alcohol[6] are said to dissolve the iron chloride in a mixture of iron and aluminum chlorides without dissolving much aluminum chloride.

[1] WEAVER, V. M., U. S. Pat. 1,269,236, June 11, 1918.

[2] POLLAK, J. E., Br. Pat. 103,716, Feb. 8, 1917.

[3] HUMPHREY, C. W. and D. S. McKITTRICK, U. S. Pats. 1,645,142; 1,645,143; 1,645,144, Oct. 11, 1927.

[4] PRICHARD, G. L. and H. HENDERSON, U. S. Pat. 1,641,503, Sept. 6, 1927.

[5] HALL, F. W., U. S. Pat. 1,512,420, Oct. 21, 1924.

[6] WOLCOTT, E. R., U. S. Pat. 1,647,446, Nov. 1, 1927.

CHAPTER VIII

MATERIALS FOR THE REDUCTION PROCESS
ELECTROLYTE AND CARBON ELECTRODES

By

JUNIUS D. EDWARDS

ELECTROLYTE

Cryolite.

Cryolite is fundamentally as important as alumina in the reduction of aluminum. Its remarkable solvent power for alumina and its greater electrochemical stability are what make possible the present-day aluminum industry. The natural mineral cryolite is something of a rarity in that there is only one commercial deposit known—that in Greenland. It is quite practical, however, to make "synthetic cryolite," which is its chemical equivalent as far as the electrolytic reduction of aluminum is concerned.

Cryolite, meaning "ice rock," was so named because of its ice-like appearance. Legend has it that the Eskimos called it "an ice which would not melt in summer." The first specimens were shipped from Greenland by Sir Charles Giesecke in 1808, and were eagerly sought by mineralogists. The first commercial use of cryolite was undertaken by Prof. Julius Thomsen of Copenhagen, who developed a method of making sodium aluminate from it and used it in enamelling iron and for other purposes, such as soapmaking and dyeing. In 1854, Thomsen obtained the exclusive right to mine cryolite at Ivigtut, Greenland. The property was leased by the present operators, "Aktieselskabet Kryolith-Mine og Handelsskabet," of Copenhagen, in 1865. In the same year, the Pennsylvania Salt Manufacturing Company, (Philadelphia, Pennsylvania) made a contract with the Danish Government which gave it a monopoly of the cryolite trade in North and South America. Since then a substantial proportion of the cryolite mined has been shipped to America. Originally about two-thirds of the cryolite mined

was shipped to America and the balance to Denmark, but the greater part now goes to Denmark. In 1922, S. H. Ball estimated that some 500,000 metric tons had been mined to date. The royalties from the sale of cryolite are administered by the Danish Government for the welfare of the native population of Greenland, which is far from self-supporting.

The Danish Government, in their series, "Meddelelser Om Grønland," have, through a long period of years, published accounts of the natural resources of Greenland. Volume 63 (1923) contains an account by Sydney H. Ball of "The Mineral Resources of Greenland" (in English), which includes a description of the cryolite mines at Ivigtut.[1]

Ivigtut, where the cryolite deposit is located, is on Arsuk Fjord, about 13 miles inland, and not far from the southern tip of Greenland. The mine itself is a large open quarry at the water's edge and is separated from the fjord by an embankment about 50 feet wide. The open pit is more than 150 feet deep. The cryolite is loosened from the walls by air drilling and blasting. It is then hauled to the top of the embankment where it is sorted ready for loading. The ships on which the cryolite is loaded tie up to the embankment where the cryolite is piled. Preparatory to sorting, it is wet down with water, since the difference in the refractive indices of quartz and cryolite is sufficient to permit ready separation by hand sorting. The refractive indices of cryolite, being close to that of water, make it seem dull in comparison with quartz when the two minerals are wet. Colored minerals and rock are, of course, easily distinguished and separated at the same time. The cryolite deposit is associated with much pegmatitic material and lies within a small intrusive mass of porphyritic granite. Associated minerals are largely quartz, siderite, galena, sphalerite, chalcopyrite, and pyrite.

The operation of mining cryolite is a hazardous one. The miners swing from the face of the cliff by long ropes while drilling and blasting cryolite. They are picked men, many from the Danish army, and are engaged for a term of a year and a half, although some of the men are reëngaged for term after term.

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[1] Samuel G. Gordon has also published in *Eng. Mining J.-Press*, **121**, 236 (1926), an account of a visit to Ivigtut. The "Saga of a Supercargo" (Macrae Smith Company, Philadelphia), by Fullerton Waldo, recounts in narrative form a trip to Ivigtut made on a freighter sailing from Philadelphia for a load of cryolite.

'or several months in the long winter, the sun does not rise ,bove the hills at Ivigtut and no boats arrive. The long and onesome winters are somewhat alleviated since the coming of adio broadcasting. During the winter, a reduced staff is mployed in stripping the overhanging granite walls and pre-)aring for the coming season. The mining season is about 7 nonths long, but is largely governed by the length of time in vhich water can be used in sorting without freezing to the cryolite.

The crude cryolite is prepared for the market by first crushing, o that it will all pass a ¼-inch mesh, after which it is passed)ver wet concentrating tables which separate out a considerable)ortion of the impurities. The cryolite concentrates are then lried and passed through magnetic separators which remove ,he greater part of the iron impurities remaining in these con-:entrates. This final purified cryolite is then ground.

Synthetic Cryolite.

The aluminum industry is not dependent upon the Greenland leposits for its supply of cryolite, since cryolite can be readily nade synthetically. The simplest processes for the production of synthetic or "artificial" cryolite, as it is sometimes called, nvolve the neutralization with hydrofluoric acid, of soda and ilumina in the proportions occurring in cryolite, Na_3AlF_6. The reaction may, in principle, be represented as follows:

$$3Na_2O + Al_2O_3 + 12HF = 2Na_3AlF_6 + 6H_2O.$$
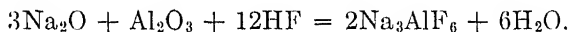
One such process employs as a source of soda and alumina the sodium aluminate solution produced in the Bayer process.[1] Sodium aluminate itself presumably has the formula, $Na_2Al_2O_4$, or $Na_2O.Al_2O_3$, but the sodium aluminate liquor carries excess alkali and this can be adjusted to the proper proportion for the production of cryolite. Sodium carbonate can also be used to supply the soda content, and aluminum hydrate the alumina content of the cryolite. By varying the ratio of soda and alumina it is possible to make mixtures of cryolite ($3NaF.AlF_3$) and chiolite ($5NaF.3AlF_3$), or mixtures of cryolite with either excess sodium fluoride or aluminum fluoride. An alternative method is to neutralize a solution of aluminum fluoride and hydrofluoric acid with sodium carbonate, or precipitate cryolite from such a solution with some other sodium salt.

[1] LAGE, H., Fr. Pat. 419,290, Dec. 30, 1910.

The fluorine for synthetic cryolite is obtained from fluorspar. Hydrofluoric acid is first made by treating fluorspar with sulphuric acid in suitable iron kilns.[1] The mixture of ground fluorspar and sulphuric acid is continually stirred while passing through the heated iron kiln, and the hydrofluoric acid which is liberated is absorbed in water in suitable cooling and absorbing towers.

The insoluble cryolite formed by the reaction of hydrofluoric acid with alumina and soda is dried and lightly calcined to remove the water. Heating cryolite at relatively high temperatures in the presence of water results in partial hydrolysis with the formation of alumina and the liberation of fluorine as hydrofluoric acid. It is quite essential, therefore, that the cryolite be carefully dried and calcined under conditions which minimize the loss of fluorine.

The processes just described employ previously purified materials for the production of cryolite. There are available large supplies of fluorspar containing silica as an impurity in substantial amounts. Hydrofluosilicic acid and its sodium salts are readily produced from such material, and various processes have been suggested to utilize these materials in the production of cryolite.[2] It has been proposed, for example, to digest sodium fluosilicate with some form of alumina with the production of cryolite according to the following reaction:

$$2Na_2SiF_6 + Al_2O_3 + Na_2CO_3 = 2Na_3AlF_6 + CO_2 + 2SiO_2.$$
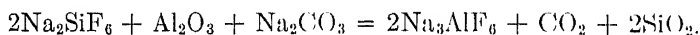
The cryolite is, however, contaminated with silica, although claims have been made that it could be held in colloidal condition and filtered off.

[1] Bishop, H. B., U. S. Pat. 1,150,415, Aug. 17, 1915; E. S. Fickes, U. S. Pats. 1,288,400, Dec. 17, 1918, and 1,316,569, Sept. 23, 1919.

[2] Richters, E. R., Br. Pat. 15,394 (1890); U. S. Pat. 417,063, Feb. 24, 1891.

Humann and Teisler, Br. Pats. 27,231 (1909); 12,626, Nov. 28, 1913; U. S. Pat. 1,015,220, Jan. 16, 1912; Ger. Pats. 289,064, Dec. 1, 1915; 293,944, Aug. 31, 1916; 348,274, Feb. 3, 1922; Fr. Pats. 108,131, Mar. 18, 1910; 458,750, Oct. 17, 1913; 461,181, Oct. 23, 1913; Aust. Pat. 46,381, Feb. 10, 1911; Norw. Pat. 26,279, Oct. 4, 1915; Swiss Pat. 65,132, May 5, 1913.

Chem. Fab. H. Bergius and Co., Ger. Pat. 307,525, Aug. 29, 1918.

Buchner, M., Br. Pat. 234,852, July, 29, 1926.

Sander, F., U. S. Pat. 1,642,896, Sept. 20, 1927.

Reich, J., Br. Pat. 21,073 (1897) Nov. 27, 1897.

Sellar, W. C., Br. Pat. 11,753 (1900) May 11, 1901.

Another type of process involves the direct digestion of calcium uoride with aluminum sulphate to produce a solution containing substantial portion of the fluorine as the hypothetical aluminum uosulphate, $Al_2F_4SO_4$.[1] Cryolite is to be precipitated from the uosulphate solution by the addition of a sodium salt and acid. Iowever, none of these processes seem to have had any extensive ommercial application, so it may be assumed that they do not vork as well in the factory as they do "on paper."

Physicochemical Relations of Fused Fluorides.

In speaking of the Hall process, it is customary to describe t as depending on the electrolysis of a solution of alumina in *ryolite.* Hall not only discovered the fact that cryolite would lissolve alumina, but made the general observation that many other combinations of aluminum fluoride with the fluorides of iodium, potassium, lithium, and calcium would dissolve alumina n substantial quantities and could be used as electrolyte.[2] This offered means of usefully varying the fusibility, conductivity, lensity, and other properties of the fused electrolyte. A proper

[1] GRABAU, Ger. Pat. 48,535, Mar. 8, 1889; Br. Pats. 13,564 (1886) Oct. 25, 1887; 14,356 (1887) Aug. 24, 1888; U. S. Pat. 386,704, July 24, 1888; A. G. BETTS, U. S. Pat. 1,598,672, Jan. 9, 1922.

For other processes see also:

GRÄTZEL, R., Br. Pat. 156, Jan. 5, 1885; Swed. Pat. 415, Aug. 26, 1886; Can. Pat. 22,779, Nov. 5, 1885; U. S. Pat. 338,061, Mar. 16, 1886.

PIEPER, CARL, Ger. Pat. 35,212, Apr. 5, 1886.

JACQUEMART, F., Br. Pat. 4,204, Dec. 22, 1873.

MATTHEWS, D., Br. Pat. 11,963, Mar. 8, 1899.

GRIESHEIM-ELEKTRON, Br. Pat. 203,708, Aug. 21, 1924; Swiss Pat. 107,615, Nov. 1, 1924; Swiss Pat. 108,188, Dec. 16, 1924.

LOSEKANN, G., U. S. Pat. 969,381, Sept. 6, 1910; Br. Pat. 19,738 of (1908); Can. Pat. 119,484, July 20, 1909; Ger. Pat. 205,209, Dec. 19, 1908; Fr. Pat. 396,703, Apr. 19, 1909; Aust. Pat. 40,175, Dec. 27, 1909; Swed. Pat. 26,682, Apr. 17, 1909; Swiss Pat. 46,039, Nov. 23, 1908.

HOWARD, H., U. S. Pats. 1,475,155; 1,475,156; 1,475,157; 1,475,158, Nov. 20, 1923; 1,511,561, Oct. 14, 1924.

SPECKETER, H., J. SÖLL, and R. BILFINGER, U. S. Pats. 1,517,686, Dec. 2, 1924; 1,548,639, Aug. 4, 1925; SPECKETER, U. S. Pat. 1,563, 536, Dec. 1, 1925.

MILLS, W., Br. Pat. 20,377 (1895) Sept. 5, 1896; Ger. Pat. 94,849, Oct. 30, 1897.

CHEMISCHE FAB. GRIESHEIM-ELEKTRON, Norw. Pat. 41,202, Apr. 14, 1925; Fr. Pat. 570,637, May 5, 1924.

[2] HALL, CHARLES MARTIN, U. S. Pats. 400,664, 400,665, 400,666, Apr. 2, 1889.

interpretation of the electrolytic process requires some knowledge of the physicochemical relations in these systems.

The System Sodium Fluoride–Aluminum Fluoride.

The most reliable published observations on the system sodium fluoride-aluminum fluoride appear to be those of Fedotieff and Iljinsky.[1] Their data on the freezing points of mixtures of these two compounds are given in Fig. 49.   Pure sodium fluoride melts at about 990°C. and cryolite at 1000°C.   There is a maximum in the freezing point curve corresponding to the mixture having the composition of cryolite or $3NaF.AlF_3$.   The addition of either sodium fluoride or aluminum fluoride to cryolite results in a lowering of the freezing point.   With sodium fluoride a eutectic mixture is formed, which contains 76 per cent sodium fluoride and 24 per cent aluminum fluoride, or 40 per cent sodium fluoride and 60 per cent cryolite.   The eutectic mixture freezes at 885°C. The addition of aluminum fluoride to cryolite rapidly lowers the melting point to a minimum of 685°C. at a concentration of 63 per cent aluminum fluoride.   Cooling curves of these mixtures up to 57 per cent aluminum fluoride showed arrests at 725°C. and a point of inflection in the liquidus curve at this temperature. The data indicate the existence of another compound, $5NaF.-3AlF_3$, which corresponds with the composition of the mineral chiolite.   According to the diagram, when mixtures containing cryolite and aluminum fluoride are allowed to cool, cryolite separates from the liquid until a temperature of 725°C. is reached. At this temperature, the cryolite which has crystallized from the liquid reacts with the excess aluminum fluoride, which has been concentrated in the liquid to form chiolite as follows:

$$5(3NaF.AlF_3)(\text{crystals}) + 4AlF_3(\text{liquid}) \rightleftarrows 3(5NaF.3AlF_3)$$
$$(\text{crystals}).$$
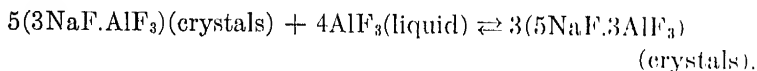
When such a solid mixture is melted, the compound chiolite

[1] Fedotieff and Iljinsky, *Z. anorg. Chem.*, **80**, 113 (1913).
See also Pyne, *Trans. Am. Electrochem. Soc.*, **10**, 63 (1906).
    Moldenhauer, *Metallurgie*, **6**, 14 (1909).
    Lorenz, Jabs and Eitel, *Z. anorg. Chem.*, **83**, 39, 328 (1913).
    Puskin and Baskow, *Z. anorg. Chem.*, **80**, 113 (1913).
    Pascal, *Z. für Elektrochem.*, **19**, 610 (1913).
    Pascal and Jouniaux, *Revue Métallurgie*, **11**, 1069 (1914); (I) *Bull. Soc. Chem.*, **13**, 439 (1913).
    Roush and Miyake, *Trans. Am. Electrochem. Soc.*, **48**, 153 (1925).

lecomposes at the constant temperature of 725°C., cryolite and
aluminum fluoride again being formed.

The volatility of the mixtures of cryolite with aluminum
fluoride increases rapidly with increase of the aluminum fluoride
content, and above about 65 per cent the mixtures were too
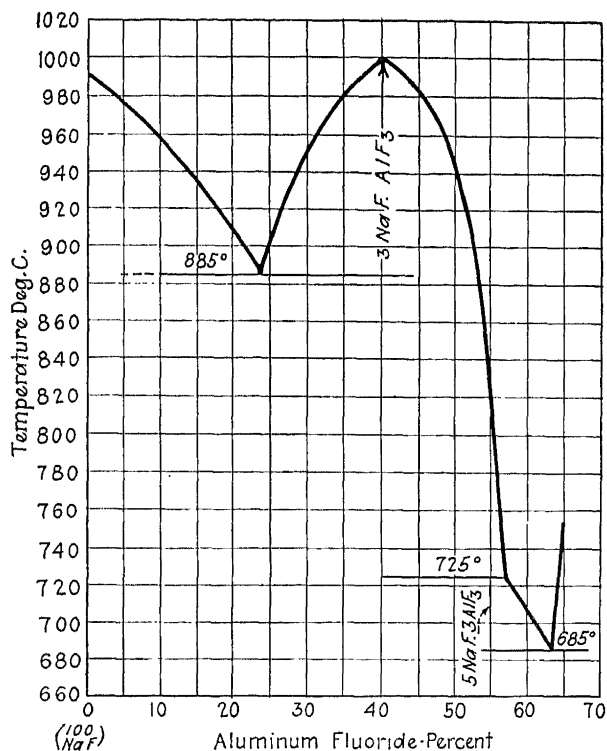
Fig. 19. Diagram of freezing points in the system sodium fluoride-aluminum
fluoride.

volatile to permit accurate observation. Pure aluminum
fluoride sublimes at high temperatures and Fedotieff and Iljinsky
prepared the pure compound for their work by sublimation.

The Ternary System: Sodium Fluoride-Calcium Fluoride-Aluminum Fluoride.

Calcium fluoride has been recommended as an addition to
fused cryolite because of its action in lowering the freezing point.
A certain amount of it tends to accumulate in the bath on account

of the presence of lime in the ash of the electrodes. Fedotieff and Iljinsky[1] have also published the results of their investigation of this ternary system. The diagram of the ternary system shows, in triangular coördinates, the isotherms or lines of constant freezing point (Fig. 50.). The shaded areas were not explored, so that it was not definitely ascertained whether there was a double compound of aluminum fluoride and calcium fluoride. There is a eutectic mixture of the two freezing at 820°C. and having the composition of 61 per cent calcium fluoride, 39
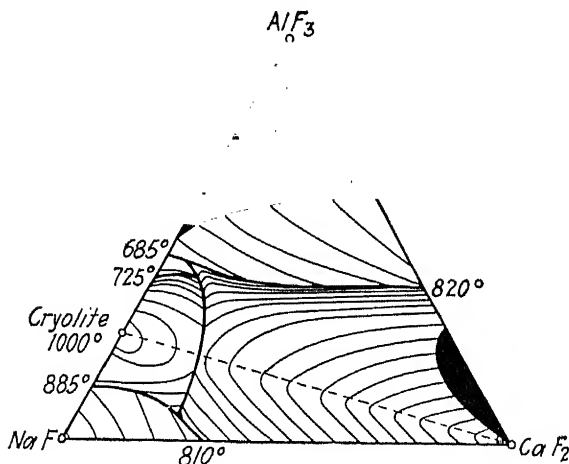
Fig. 50.—Diagram of freezing points in the system sodium fluoride-aluminum fluoride-calcium fluoride. (Compositions plotted in mol-per cent.)

per cent aluminum fluoride. Sodium fluoride and calcium fluoride also form a eutectic mixture freezing at 810°C. and having the composition 53 per cent sodium fluoride, 47 per cent calcium fluoride.

The dotted line shows the compositions having sodium fluoride and aluminum fluoride present in the concentration corresponding to the compound cryolite, and it is compositions in the neighborhood of this line that are of principal interest in connection with the electrolyte for the aluminum process. It is of interest to note, however, that with excess sodium fluoride, the lowest melting point is given by the ternary eutectic freezing at 780°C. With excess aluminum fluoride, there are invariant points at 705°C. and 675°C.

[1] FEDOTIEFF AND ILJINSKY. Z. anorg. Chem., **129**, 93 (1923).

Solubility of Alumina in Cryolite.

The solubility of alumina in cryolite and other fluoride mixtures is very important, and the literature contains many contradictory statements regarding their solubility relations. The freezing point curve of mixtures of alumina and cryolite, as determined by Fedotieff and Iljinsky, is given in Fig. 51. The freezing point of cryolite is lowered by additions of alumina until a content of about 16 per cent is reached. Apparently there is a eutectic mixture corresponding to this composition which freezes at 935°C. Further additions of alumina rapidly raise the
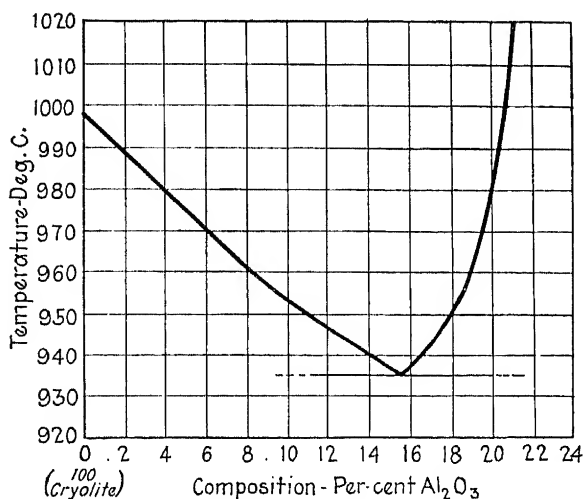
FIG. 51.—Diagram of freezing points in the system cryolite-alumina.

freezing point so that a saturated solution at 1000°C. contains only about 21 per cent of alumina. As a matter of fact, great difficulty is found in completely dissolving 20 per cent of alumina in cryolite at 1000°C.

Fedotieff and Iljinsky did not determine the complete freezing point curve of alumina with the system sodium fluoride-aluminum fluoride, but made the qualitative observations that when the melt contained sodium fluoride in excess of the cryolite ratio, the solubility of alumina was appreciably increased. The eutectic mixture of cryolite and sodium fluoride (60 per cent cryolite, 40 per cent sodium fluoride) is saturated with 20 per cent alumina at about 890°C., and holds a substantially greater

quantity in solution at 1000°C. The solubility of alumina decreases from the eutectic mixture to pure sodium fluoride, in which alumina is completely insoluble. When cryolite contains aluminum fluoride in excess of the cryolite ratio, the solubility of alumina is decreased. Chiolite ($5NaF.3AlF_3$) dissolved only about 10 per cent alumina at 1000°C.

Fedotieff and Iljinsky found that binary mixtures of calcium fluoride and aluminum fluoride had only a low dissolving power for alumina. They stated that the eutectic mixture would not dissolve 5 per cent alumina. Adding calcium fluoride to cryolite, they found that the mixture with 10 per cent calcium fluoride dissolved 10 per cent alumina easily and the freezing point was lowered to 910°C. With 20 per cent calcium fluoride, the solubility of alumina was substantially less, their statement being that 10 per cent alumina could be dissolved with "continued heating."

Electrical Conductivity.

Kurt Arndt and Wilhelm Kalass[1] have made a series of conductivity measurements on fused mixtures of cryolite and alumina. The absolute values are in question, since they report a melting point for cryolite of 979°C., whereas pure cryolite melts at 1000°C.; this indicates either an impure material or some error in the temperature measurements. The relative values, however, are of interest. They found that the addition of alumina to cryolite lowered the conductivity and that the lowering was proportional to the amount added. At 1000°C., they reported a specific conductivity of 2.23 reciprocal ohms per centimeter cube for cryolite, and 1.80 reciprocal ohms per centimeter cube for cryolite with 20 per cent alumina added. Mixtures having sodium fluoride in excess of the cryolite ratio showed a slightly higher conductivity than cryolite. The experiments with cryolite and excess aluminum fluoride were not very successful, but they concluded that the addition of aluminum fluoride did not materially change the conductivity.

CARBON ELECTRODES

Carbon may be properly considered to be one of the raw materials used in the production of aluminum, for the carbon

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[1] *Z. für Elektrochem*, **30**, 12 (1924).

electrodes used to lead the current into the electrolyte are oxidized and consumed in the process; in fact, for each pound of aluminum produced, about three-quarters of a pound of carbon is consumed. The requirements for a satisfactory carbon electrode are numerous. The first requirement is that the carbon electrode shall be as free as possible from impurities; the ash of the electrode is dissolved by the electrolyte, and the oxides of iron and silicon will be reduced and appear as metallic impurities in the aluminum. Any lime and magnesia in the ash will accumulate in the electrolyte. In addition, the electrode should have high electrical conductivity in order to minimize power losses. It should show a slow rate of oxidation at high temperatures and have as low a thermal conductivity as is consistent with its other properties. The electrode should be rugged and possess the necessary strength to permit its handling and use without cracking, chipping, or breaking. Finally and obviously, its cost should be as low as possible.

Carbon electrodes are made from a mixture in suitable proportions of carbon, in the form of coke, and a binding agent. The electrodes fashioned from this mix are then heated to a high temperature to eliminate all volatile matter and produce a hard, rugged, carbonaceous electrode. Because of the essential requirement of purity, it is customary to use petroleum coke or specially prepared anthracite coke in the manufacture of electrodes for the aluminum reduction process.

Petroleum coke is particularly adapted for electrode manufacture because it has a very low ash content, usually about 0.5 to 1.0 per cent, is high in fixed carbon, and has the necessary strength and hardness. It is obtained as a residue in the distillation of crude oil and is received from the oil refineries in pieces of irregular size and shape. The content of volatile matter varies considerably with the distillation practice and may run from 4 to 20 per cent. The first step in the manufacture of electrodes is to crush the coke by passing it through roll crushers, after which it may be screened. It is then ready for calcination.

Pitch coke, a product of the destructive distillation of pitch, is also used in substantial amounts in place of petroleum coke, which it closely resembles. Pitch coke made by some processes is sufficiently low in volatile matter to permit its use directly in the electrode mix without a preliminary calcination. Its purity is comparable with that of petroleum coke.

The best anthracite coals for electrode manufacture have a hard, dense structure and are relatively low in volatile content and ash. Welsh anthracite is available with ash as low as 1.3 to 4.0 per cent, but the American anthracite generally runs somewhat higher. It is possible by wet concentration to decrease the ash content somewhat, but such treatment is not usually employed with the Welsh anthracite. The smaller sizes of anthracite are used for electrode manufacture and are usually calcined without previous crushing.

Calciners.

The object in calcining the coke or anthracite is to remove the volatile constituents and to "shrink" it to increase its density. For the calcination of coke, the gas-heated calciner has been generally employed, although the electrically heated calciner has found some application. The principle of the continuous gas-heated retort is illustrated by the diagram of Fig. 52. The crushed petroleum coke is fed through a hopper system in the top of a tall, vertical retort. As the "green" coke, which is the term customarily applied to the uncalcined coke, is heated in its descent through the tapered retort, the volatile gases are driven out and pass up through the charge at the top, where they are taken off. The coke is cooled at

Combustion Chamber
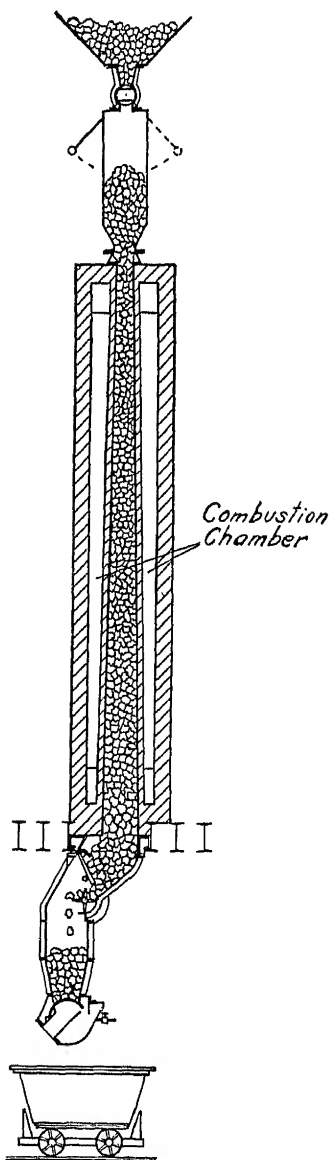
FIG. 52.—Diagram of gas calciner for calcining coke.

he bottom of the retort and removed through an automatic conveying system. Relatively high temperatures of 900 to 1100°C. are necessary in the retort for the proper shrinking of the coke. The fuel for heating the retorts is obtained from gas-producers and from the gas driven off from the coke during the calcination process.

Gas-heated calciners are expensive to maintain because of the relatively short life of the refractories under the conditions of operation. The use of electric calcining furnaces, therefore, has many advantages where power costs are low enough. The simplest type of electric calciner is intermittent in operation and consists of an upright cylindrical steel shell lined with refractory brick. The bottom of the steel shell is covered with a baked carbon electrode mix in which conductors are imbedded and which is connected to one busbar so as to serve as one electrode for the furnace. A series of cylindrical carbon electrodes are suspended in the calciner and connected by cable to the other busbar. In operation, the suspended electrodes are lowered until arcs are formed with the bottom carbon electrode. The coke which is to be calcined is then fed in around the electrodes and gradually heated until it becomes conductive. As the calcining process proceeds, the electrodes are raised from time to time and additional green coke fed in. After the shell has been filled and the heating has been continued for a sufficient time, the current is shut off and the contents allowed to stand so that the volatile matter in the coke will largely escape and the charge will reach a uniform condition. Further standing permits the cooling which must necessarily take place before the heated coke can be unloaded.

The continuous electric calciner offers many advantages over the intermittent type just described. An electric calciner[1] of the continuous type is shown in Fig. 53. The green coke is fed continuously down a vertical shaft and is heated by the passage through it of an electric current, introduced by upper and lower electrodes, as shown in the drawing. The gas formed during the calcination process is scrubbed to remove tar or wax and part of it recirculated through the furnace. The cold gas entering the bottom of the shaft cools the coke to the point where it can be safely discharged into the automatic conveyor. This gas is then heated during its passage through the furnace and

[1] HOOPES, WILLIAM, U. S. Pats. 1,366,457, 1,366,458, Jan. 25, 1921.

serves at the upper end to preheat the entering coke, so as to make it electrically conducting. Careful sizing and charging of the green coke is necessary in order to ensure uniform conductivity and hence uniform calcination of the charge. An improved form of continuous electric calciner, adapted to large scale operation, has been invented by F. C. Frary and V. C. Doerschuk.[1]
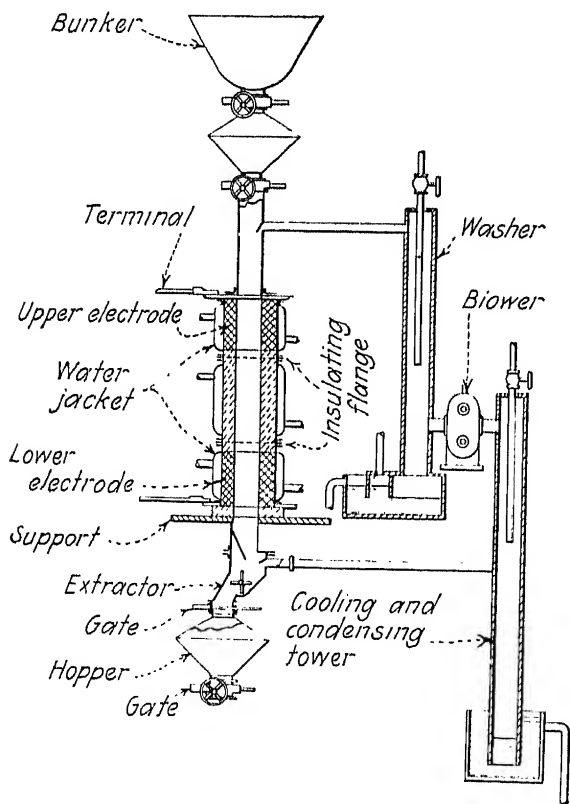
FIG. 53.— Diagram of electric calciner for calcining coke.

The calcined coke will have its density increased to about 1.9 to 2.0 and its content of volatile matter reduced to less than 0.5 per cent. The temperature of calcination should be carefully controlled so that the coke is not graphitized; graphitized material is undesirable in the electrode because it increases the thermal conductivity of the electrode to too great an extent.

[1] FRARY and DOERSCHUK, U. S. Pat. 1,671,673. May 29, 1928.

In Europe, the shaft calciner is in rather general use for the calcining of coke or anthracite coal. In this type of calciner, air is blown through the charge which is descending through the furnace shaft; by the combustion of about 20 per cent or more of the charge, sufficient heat is obtained to calcine the remainder. This type of calciner requires accurate control to produce a uniform and satisfactorily calcined product and has the disadvantage of burning more material than the other types, and consequently increasing the ash content of the calcined coke or anthracite. However, because of the lower cost of installation, under some conditions it is the most economical type of calciner.

Production of Electrodes.

The binding materials ordinarily employed in the production of electrodes are tar and pitch. Tar is the more fluid material of the two, and is used largely to give plasticity to the electrode mix. Pitch is a semi-solid product and forms the principal binding agent. A minimum of binding agent is employed, since any volatile matter in the tar and pitch will be driven out in the baking of the electrode, and it is desirable to have the electrode as dense and free from porosity as possible in order to minimize burning during use. Apparently enough binder must be used to coat each particle of carbon with a very thin film, and the carbon particles themselves should be of such graded sizes as to give a minimum of voids in the finished electrode. The relative quantities of coke, tar and pitch will, of course, vary with differences in the materials themselves. The total amount of binder used generally varies between 18 and 25 per cent, depending on the materials and the method by which the electrodes are to be made. A mixture which is to be extruded requires more binder than one which is to be shaped by pressing or tamping.

In addition to the coke and binder, two other materials are used in the electrode mix. One is green or unbaked electrode scrap, consisting of rejected electrodes and other scrap from the hydraulic presses. This has, of course, the same composition as the electrode mix and can be used in any quantity. Another material added is reclaimed electrodes from the reduction cells. The butt ends of the electrodes used up in the reduction cells are saved and worked back into the electrode mix. It is first necessary, however, to crush them and remove any metal coming from the rods used in suspending them in the cells, after which

they are pulverized and stored for use. The amount of this material which can be added to the mix must be carefully controlled.

The various ingredients of the electrode mix, properly pulverized, are stored in suitable bins from which they are weighed out in proper proportion and conveyed to a mixing machine, usually steam-jacketed. Here they are thoroughly incorporated, after which they may be reground somewhat and further mixed in edge runners or Chilean mills, or the mix may be directly
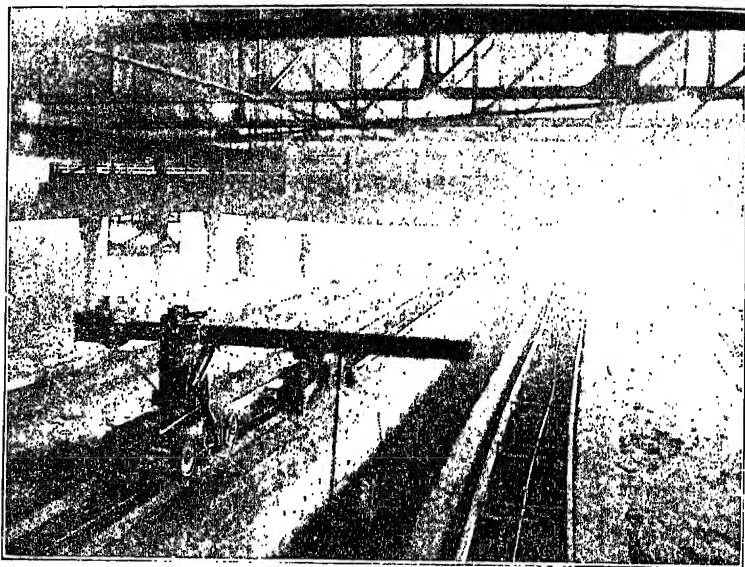
Fig. 54.—Electric furnaces for baking electrodes; furnace in center is open and being unloaded.

conveyed to the electrode presses. Electrodes, at least of the smaller sizes, are extruded under high pressure in a hydraulic press. The extruded product is cut into suitable lengths and conveyed to the baking furnaces. Electrodes of large size may be formed in molds by pressing or tamping, and this permits chamfering their tops so as to reduce the weight of unused carbon which must be returned to the process.

As in the calcination of coke, both gas-heated and electrically heated furnaces are employed for the baking of electrodes. Local conditions, such as power costs, are important factors in determining which method is most economical to use. In either

ype the electrodes are packed into a chamber and surrounded
y a granular supporting material, such as coke dust.   In the
as-heated type of furnace, the function of the carbon dust is
argely to support the electrodes so as to maintain their shape
uring the baking process.   In the electrically-heated furnace,
he charge itself must act as a resistor and carry the current.
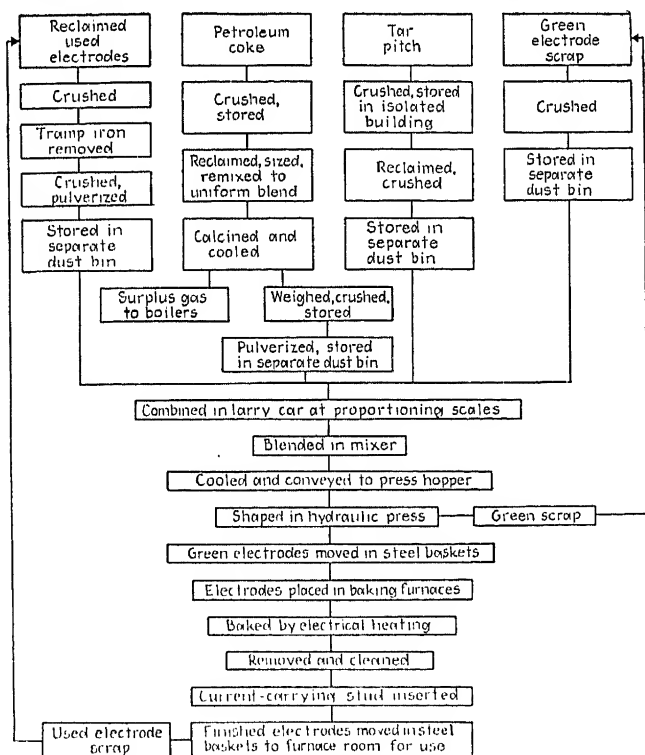
FIG. 55.-- Flow sheet of carbon electrode plant at Arvida.

The current is carried by previously baked cores until the furnace
charge is heated to the point at which it becomes conductive.   In
the baking operation, the volatile matter is driven out and the
binder carbonized.   The density of the electrode is reduced and
its electrical conductivity is substantially increased thereby.

When the baking operation is complete, the furnace is cooled
down to the point where the electrodes can be removed without
danger of burning, and without too much discomfort to the
workman, and the furnace is opened.   The electrodes are then

ready for the cleaning operation required to remove any packing material adhering to the surface of the electrodes. This can be accomplished by holding the electrodes against revolving brushes, or by tumbling them in large steel containers. The electrodes after baking are hard and rugged, and if properly made, stand a great deal of rough treatment.

The smaller sized extruded electrodes are generally cylindrical in cross-section and from 3 to 6 inches in diameter. The pressed or molded electrodes are usually square or rectangular in section and are made in sizes up to about 12 by 20 inches. The type of electrode used depends, of course, on the design and method of operation of the electrolytic cell.

The final operation in the production of electrodes consists in attaching the rod used in suspending it in the cell and which also acts as a conductor for the current. Both iron and copper rods have been used for this purpose. The copper rod has a higher conductivity and hence lower power loss, but is much more expensive than the iron rod. In the case of large pressed electrodes, a hole is molded in the unbaked electrode, and after baking, the iron or steel supporting rod or the stub to which the rod is later fastened is attached to the carbon by inserting it in this hole and casting iron around it. Copper rods are attached to the extruded carbons by drilling a hole in the end of the carbon and screwing into it a copper rod, the end of which is threaded and which cuts its own threads in the carbon. An alternative method is to ream a tapered hole in the carbon anode and drive it onto the tapered end of the metal rod.[1]

The diagram of Fig. 44[2] shows in outline the various steps employed in the production of carbon electrodes at the Arvida plant of Aluminum Company of Canada.

C. W. Söderberg has developed a so-called "continuous electrode" which is formed, baked, and continuously renewed in the furnace in which it is used. The application of the Söderberg electrode to the electrolytic production of aluminum is discussed in the next chapter.

[1] Boothman, D. M., U. S. Pat. 1,490,504, Apr. 15, 1924.
[2] McBride, R. S., *Chem. Met. Eng.*, **34**, 76–83 (1927).

CHAPTER IX

THE PRODUCTION OF ALUMINUM

By

Francis C. Frary and Junius D. Edwards

Practically all the common metals, except when they are found free in nature, are produced from their oxides by reduction, i.e., removal of oxygen. Aluminum is no exception to this rule. While it may be produced from other compounds such as the chloride, fluoride, or sulfide, the greater cost of these compounds and the difficulties involved in their decomposition make their use too expensive.

Aluminum oxide has a very much higher heat of formation than the oxides of such metals as iron, zinc, lead, copper, and tin, and this is the reason why it is so difficult to reduce.[1]

Oxide	Calories per gram molecule	Calories per gram atom oxygen
Aluminum Oxide (Al_2O_3)....	378.0	126.0
Iron Oxide (Ferrous, FeO)...............	65.7	65.7
Iron Oxide (Ferric, Fe_2O_3).....	196.5	65.5
Iron Oxide (Magnetic, Fe_3O_4)	270.8	67.7
Zinc Oxide (ZnO)........ .... '...	85.2	85.2
Lead Oxide (PbO)....	50.3	50.3
Lead Peroxide (PbO_2)	62.1	31.2
Copper Oxide (CuO)...	37.2	37.2
Tin Oxide (Stannous, SnO)	66.9	66.9
Tin Oxide (Stannic, SnO_2)	137.5	68.7

Metallic oxides with low or moderate heats of formation may be easily reduced by carbon or carbon monoxide at moderate temperatures, usually under 1000°C. (1800°F.), and a relatively simple smelting process is all that is required to produce the metal. Aluminum oxide, however, cannot be reduced at all by carbon monoxide, and is only attacked by carbon at tempera-

[1] These heats of formation are usually given in kilogram-calories per gram molecule, but to get them on a common basis we should compare the values per gram atom of oxygen:

tures above about 1800°C. (3270°F.). Such temperatures can
be obtained in an electric furnace, but they are expensive to
maintain. The principal difficulty in thus producing aluminum,
however, lies in the fact that the required temperature is so high
that the aluminum formed remains in the gaseous state, and is
carried away by the carbon monoxide formed by the reaction:

$$Al_2O_3 + 3C = 2Al + 3CO.$$
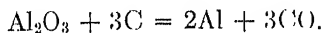
It is only by having considerable amounts of other metals, such
as copper, iron, or silicon, present to combine with the aluminum
and reduce its volatility, that metallic aluminum (in the form
of an alloy) can be recovered by smelting its oxide with carbon.

This same high heat of formation of the oxide prevents the
electrolytic deposition of aluminum from any aqueous solution
of its salts. Copper, zinc, tin, and iron can be electrolytically
deposited by passing a direct current through aqueous solutions
of their salts, but when an aluminum salt is thus electrolyzed
the metallic aluminum reacts at once with the water to form
aluminum oxide or hydroxide, and hydrogen. This may be
explained on the ground that aluminum has a greater affinity for
oxygen than has hydrogen; in other words, the heat evolved
when an atom of oxygen combines with aluminum is greater than
when it combines with hydrogen. Evidently then, in order to
electrolyze aluminum compounds, we must employ a solvent
which does not react with aluminum, and is more difficult to
decompose electrolytically than the aluminum compound we
propose to use.

Charles M. Hall,[1] reasoning and experimenting along these
lines, discovered such a solvent in the natural mineral cryolite,
which is a double fluoride of sodium and aluminum, having the
chemical formula Na_3AlF_6. This substance melts at about
1000°C., and at temperatures slightly above its melting point
is able to dissolve as much as 10 to 20 per cent of its weight of
aluminum oxide. Other fluorides may be added to the electro-
lyte to improve its behavior.[2] If a direct current be passed
through this solution, the aluminum oxide is decomposed;
aluminum is being deposited (molten, since its melting point is

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[1] HALL, C. M., U. S. Pat. 400,667, Apr. 2, 1889; Br. Pat. 5,670 (1889),
June 1, 1889; Swiss Pat. 921, May 22, 1889.

[2] HALL, C. M., U. S. Pats. 400,664 and 400,766, Apr. 2, 1889; Br. Pat.
5,669 (1889), June 1, 1889; Swed. Pats. 2361, Sept. 27, 1890 and 2,825, May
16, 1891.

bout 660°C.) at the cathode or negative pole, while oxygen is
eposited at the anode or positive pole.

In practice this positive pole is made of carbon, and the
xygen at once combines with it.   It is probable that the primary
roduct at the anode is carbon dioxide, more or less of which is
ubsequently reduced to carbon monoxide by the hot carbon.
he oxidation of the carbon anodes by the electrodeposited
xygen adds a substantial amount of heat and in effect reduces
e amount of electric energy required to maintain the fused
ath at the proper temperature.

Both fused cryolite and molten aluminum are extremely
active at the temperature at which the electrolysis takes place,
d therefore the problem of a container is a serious one.   Hall
lved it by using an iron crucible lined with carbon, and the
dustry has found nothing better as far as materials are con-
rned, although of course the form and mechanical construction
the cell have undergone extensive development, and there are
any different types in use.

he Electrolytic Cell.

Broadly, a cell for the electrolytic production of aluminum
mprises a strong steel box, either rectangular or circular in
ape, provided with a carbon lining 6 to 10 inches or more in
ickness.   The diagram of Fig. 56 shows the characteristic
atures of the electrolytic cell and their relation to each other.
he steel plate used is from 1 to 2 inches thick, and generally
akes contact, either directly or through collector plates, with
e carbon lining, so that the steel shell may be used to carry the
rrent to the carbon cathode.   In some cells heavy steel
stings, located within and insulated from the steel shell, are
ed to make contact with the carbon lining.   In such a case,
e end of the casting projects through an opening in the steel
ell, and the current-carrying cables are bolted to it.   In some
ses insulating material is used between the carbon lining and the
ell, serving the double purpose of retaining heat in the cell
d thus (presumably) reducing the power required to maintain
at the proper temperature, and lowering the temperature of the
eel shell so that it is easier for the workman to attend to
e cell.   There seems, however, to be some difference of opinion
nong operators as to the real advantages of such thermal
sulation, when all factors are considered.   Certainly, however,

heating by the auxiliary use of alternating current,[1] or of gas or other flames[2] is unnecessary and impractical.

The size of the cell and the size of the electrolyte cavity vary, depending on the number of amperes which it is intended to use in the cell. It is probably not feasible to go below about 8,000 amperes; and on general principles, the more current that can be used in a cell, the lower the cost of producing a pound of aluminum. This is chiefly due to the fact that it takes practi-
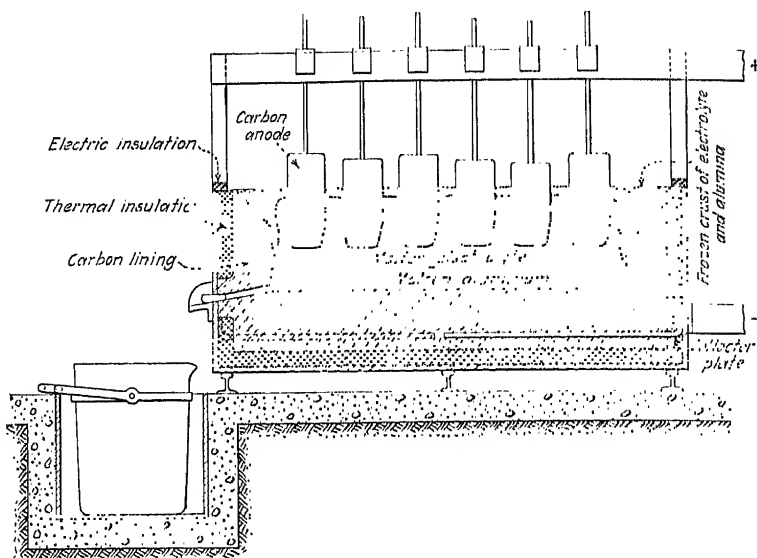
Fig. 56.—Diagram of electrolytic cell.

cally as much labor to run a small cell as it does to run a large one (of proper design), while the amount of aluminum produced per cell per day is approximately proportional to the current employed. The upper limit in the amount of current employed is set by the increasing difficulty involved in changing anodes and breaking in the frozen crust in the larger cells. It is probable that for cells with multiple electrodes this practical limit is nearly reached at 30,000 amperes, but perhaps the application of the Söderberg continuous electrode may permit the use of larger currents.

[1] ALLGEMEINE ELEKTRIZITÄTS GES., Ger. Pat. 332,669, Feb. 7, 1921.

[2] DOLTER, H., U. S. Pat. 1,580,469, Apr. 13, 1926; Br. Pat. 240,163, June 3, 1926; Ger. Pat. 447,687, July 27, 1927.

The carbon lining of the electrolytic cell is of great importance.
must have adequate strength and electrical conductivity
that it will remain in place and carry the current to the
etallic aluminum. If it becomes overheated or stressed
cally it is likely to crack or disintegrate, and of course if its
rength is inadequate it is easier for it to be broken. Broken
eces of lining will float in the bath and cause trouble at times
making partial short circuits between the anodes and the
etal. Breaks in the lining also permit the aluminum to run
wn and make contact with the steel shell or lining plates,
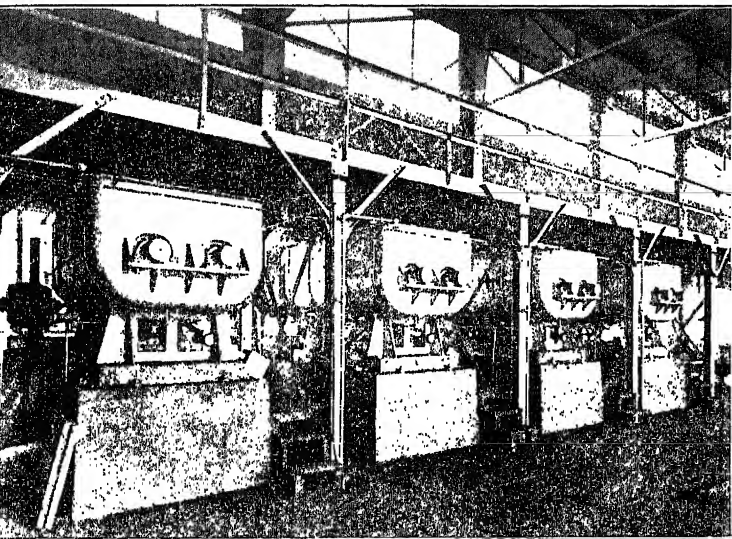
Fig. 57. Steam jacketed mixers for carbon lining for cells.

th the result that the aluminum dissolves the iron and is
ntaminated to such an extent that the cell must be shut down
d the lining replaced. This involves a considerable expense,
t only on account of the labor involved but also because of the
ct that the porous carbon lining absorbs somewhere near its
wn weight of the fused electrolyte; and since it is impossible,
general, to patch such a lining, throwing away the lining
volves the loss of a considerable amount of cryolite. In
ddition, when a cell is first put into operation with a new lining,
s metal output is low for the first week or two, and in general
e quality of the metal is not up to standard because of con-
mination from ash of the coke used in the lining.

Evidently the proper lining of the electrolytic cells is a matter of great importance to the aluminum producer. There are two types of lining used. One is made by ramming into the steel shell a hot mixture of pulverized coke with tar and pitch, using a suitable cast-iron form to give the cavity the desired shape, and then baking the whole in a furnace at about 600 to 800°C. The other method involves building up the lining out of carbon blocks which have been preformed and baked in the same way that the electrodes are manufactured, cementing these blocks together with a mixture of tar, pitch, and ground coke. In either case, great pains are taken to produce as durable a lining as possible so as to give the cell as long a life as possible and thus reduce the plant expense for relining. A cell may run from 1 week to 3 years before it is necessary to line it. It also has been proposed[1] to use graphite blocks for lining the cells, but this lining would be very expensive.

The carbon anodes are likewise made of a mixture of carbon, pitch, and tar, stamped or pressed into molds or extruded through a die, and subsequently baked at 1000°C. or more. Because ordinary coke contains a relatively large amount of silica and iron oxide in its ash, which would contaminate the metal made, it is customary to employ petroleum coke or else a special low-ash anthracite, or both, to furnish the carbon.

Two or more copper or aluminum busbars are supported above the electrolyte cavity of the cell, and the anodes hang from these and dip into the molten cryolite electrolyte. They are supported by rods or bars of copper, aluminum, or iron, which are clamped onto the busbar and not only support the anodes mechanically but also carry current to them. One of the important factors in the operation of the cell is the adjustment of these anodes so as to properly divide the current among them. If an anode is set too low, a projecting point may touch the metal layer in the bottom of the cell and allow part of the current to pass directly to the metal without passing through the electrolyte, and thus without producing any aluminum. If the anode is set too high, the resistance of the thicker layer of electrolyte between it and the cathode will prevent it from taking its share of the current and, consequently, increase the load on the other anodes.

[1] LAUBER, E. R., Swiss Pat. 121,860, Aug. 1, 1927; Span. Pat. 98,527, June 26, 1926; Ger. Pat. 452,895, Nov. 22, 1927; Fr. Pat. 618,356, Mar. 8, 1927.

öderberg Continuous Electrode.

C. W. Söderberg has invented and developed a continuous lf-baking electrode which has interesting possibilities. Its iginal applications were in the electric furnace production of lcium carbide and ferro-alloys, but its application to the ectrolytic reduction of aluminum is now being developed. he Söderberg electrode consists essentially of a cylindrical etal mantle or casing extending from the furnace to a platform cated directly above the furnace.[1] This mantle is filled with e carbonaceous mixture constituting the body of the electrode. he mantle serves as a mold to hold and support the carbon ix during the baking operation. It also protects the carbon om oxidation and helps carry the current. The electrode ix at the lower end is gradually baked by the heat from the rnace as well as by the current passing through the mantle and rough the carbon of the electrode, where it has baked suffi- ently to become electrically conducting. In operation, as the ectrode with its enclosing mantle is consumed at its lower end the furnace, the electrode is lowered. The baking operation thus continuous, as the soft electrode mix gradually becomes otter and hotter in approaching the furnace zone. From time time, as necessary, a new section is welded or riveted to the p of the mantle and filled with warm, soft electrode paste.

The diagram of Fig. 58 illustrates, in principle, the application the Söderberg electrode to the production of aluminum.

[1] SÖDERBERG, C. W., U. S. Pat. 1,440,724, Jan. 2, 1923; Can. Pat. 216,092, b. 21, 1922; Br. Pat. 137,811, Mar. 11, 1920; Fr. Pat. 503,309, June 8, 20; Ger. Pat. 324,711, Sept. 2, 1920; Norw. Pat. 32,919, Aug. 15, 1921; iss Pat. 85,110, May 17, 1920; Ital. Pat. 234,795, Sept. 4, 1925; Span. t. 70,792; Czecho-Slav. Pat. 12,985; Holland Pat. 7626; Br. Ind. Pat. 11; Jugo-Slav. Pat. 4,635; Belg. Pat. 282,551; Aust. Pat. 81,162; Austral. t. 13,033; Rouman. Pats. 7,102; 8,100; Swed. Pat. 62,315; Luxemburg t. 13,063; Portug. Pat. 10,983; Hung. Pat. 85,815; Polish Pat. 3,028; rgentine Pat. 17,104; Braz. Pat. 11,767; Chilian Pat. 4,190; Mex. Pat. ,160; Chinese Pat. 23,455; Jap. Pat. 60,501; New Zealand Pat. 12,676; uth Afr. Pat. 824/19; Belg. Congo Pat. 1,129.

SÖDERBERG, C. W., U. S. Pat. 1,441,037, Jan. 2, 1923; Can Pat. 215,697, b. 7, 1922; Br. Pats. 116,835, June 27, 1918; 119,018, Sept. 19, 1918; . Pat. 488,778, Nov. 14, 1918; Ger. Pat. 317,690, Jan. 2, 1920; Swiss t. 78,851, Sept. 2, 1918; Norw. Pats. 28,799, May 13, 1918; 32,041, ay 1, 1917; Swed. Pats. 44,902; 49,506; Czecho-Slav. Pat. 16,661; go-Slav. Pat. 1,973; Belg. Pat. 281,536; Aust. Pat. 82,558; Ital. Pat. 478/ 8; Portug. Pat. 10,932; Span. Pat. 70,439; Polish Pat. 1,221; Argentine t. 17, 103; Braz. Pat. 11,766; Mex. Pat. 19,159; Jap. Pat. 44,334.

Instead of a multiplicity of electrodes, as in the customary type of cell, only one Söderberg electrode is employed per cell. Since the mantle is consumed together with the carbon interior, it should be designed so as to introduce a minimum of impurity into the aluminum. From the standpoint of low cost, a thin sheet-iron mantle has much to recommend it but, in ordinary
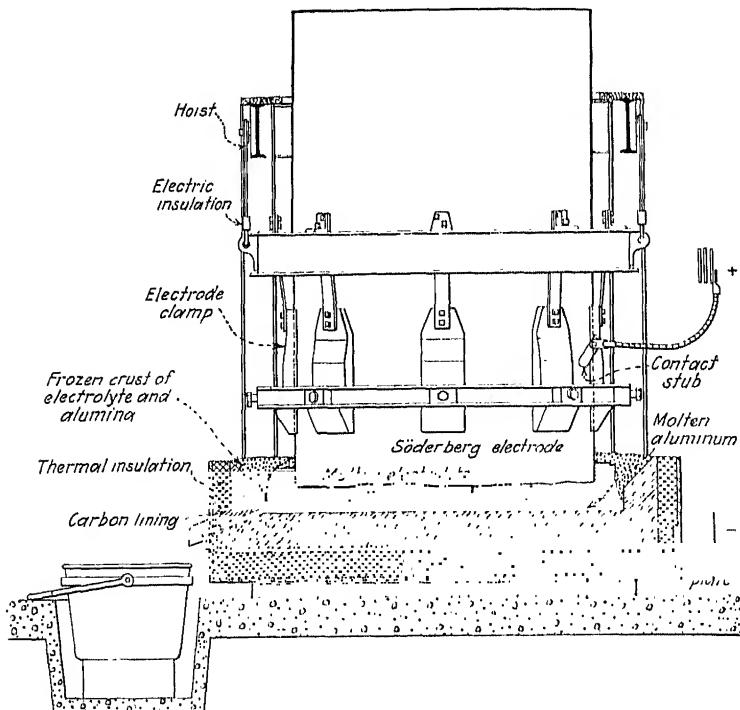
Fig. 58.— Diagram of electrolytic cell with Söderberg electrode.

operation of the electrode, it will appreciably increase the iron content of the aluminum. Westly[1] has devised a scheme of using a thin sheet-iron mantle and stripping it from the electrode before it enters the electrolytic cell. A simpler method is to make the mantle of aluminum; its lower end is gradually melted off in the cell and the aluminum recovered when the cell is

[1] WESTLY, J., U. S. 1,657,948, Jan. 31, 1928; Br. Pat. 227,822, Aug. 13, 1925; Fr. Pat. 589,997, June 9, 1925; Norw. Pat. 41,050, Mar. 9, 1925; Swiss Pat. 112,299; Swed. Pat. 60,102; Ital. Pat. 684/114; Ger. Pat. 425,443; Jugo-Slav. Pat. 3,448; Br. Ind. Pat. 10,915; Austral. Pat. 21,366; New Zealand Pat. 21,366.

pped. Current is led into the mantle and the interior of the
ectrode by suitable contact stubs attached to the mantle and
bs extending into the electrode mass.[1] Only one lead is shown
the diagram, but in practice a number are placed circumferen-
ally. As the electrode is consumed, the current leads are
ccessively moved to the next higher row of contact stubs.
he electrode is a heavy structure and a very substantial clamp-
g device is necessary to hold it securely and lower the electrode
m time to time to just the desired distance.[2] From time to
ne it is also necessary to raise the electrode clamps with respect
the electrode mantle to prevent their entering the cell and
ing melted off.

The electrode projects through a hole in a platform supported
ove the cell. The workmen stand on this platform while
taching new sections to the mantle and filling them with
ectrode paste. This electrode paste is a heated mixture of
rbon and tar-pitch binder. Because it is impractical to use
y considerable pressure in tamping the mix into the mantle,
is made with sufficient binder to make it fluid or at least of
ry high plasticity.[3] In this way it settles to a solid mass by
e time it reaches the baking zone. A dense baked carbon
ctrode of good conductivity is thus obtained at the lower end.

eration of Electrolytic Cell.

In operation, the cell contains a layer of molten aluminum,
ich may vary in thickness from a fraction of an inch up to 4 or 5
hes, resting on the bottom of the cell. The density of molten
uminum is 2.29 grams per cc. at 1000°C., while that of molten

Söderberg, C. W., U. S. Pat. 1,686,174, Oct. 2, 1928; Norw. Appln.
728, Sept. 19, 1925.

Vestla, J., U. S. Pat. 1,613,212, Jan. 4, 1927; Br. Pat. 227,820, June
1925; Fr. Pat. 589,995, June 9, 1925; Ger. Pat. 427,355, Apr. 6, 1926;
rw. Pat. 41,363, May 18, 1925; Swed. Pat. 60,447; Swiss Pat. 112,298;
l. Pat. 684/113; Jugo-Slav. Pat. 3,446; Br. Ind. Pat. 10,914; Jap. Pat.
589; Austral. Pat. 21,364; New Zealand Pat. 21,364.

Söderberg, C. W., U. S. Pat. 1,498,582, June 24, 1924; Can. Pat. 212,-
, May 31, 1924.

Söderberg, C. W., U. S. Pat. 1,670,052, May 15, 1928; Can. Pat.
,997, Oct. 12, 1926; Fr. Pat. 584,594, Feb. 10, 1925; Norw. Pat. 40,398.
. 1, 1924; Swiss Pat. 111,653; Swed. Pat. 62,153; Ital. Pat. 655/21;
ng. Pat. 89,782; Span. Pat. 90,266; Finnish Pat. 11,055; Jap. Pat. 64,571;
o-Slav. 3,757; S. Afr. Pat. 752/24; Belg. Congo Pat. 1,128; Holland Pat.
605; Belg. Pat. 332,318; Roum. Pat. 10,632; Egypt. Pat. 96-AJ.

cryolite is 2.095 grams per cc.[1] Consequently, the molten metal will remain at the bottom unless the cell contents are very violently agitated. The density of molten cryolite and aluminum for temperatures up to 1100°C. is shown in Fig. 59.[2] The
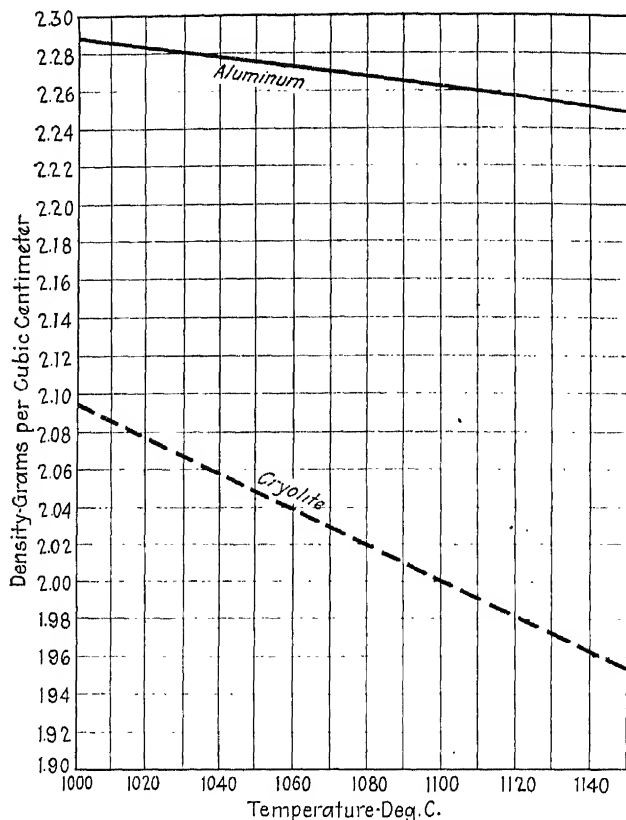
FIG. 59. Density of cryolite and aluminum between 1000 and 1100°C.

density of cryolite changes linearly with respect to temperature and does not show a maximum, as claimed by Pascal and Jouniaux.[3] Although the density of liquid cryolite increases faster than that of aluminum, with falling temperature it does not become equal to it. Solid alumina is more dense than cryolite but the solution of alumina in liquid cryolite is lighter than

[1] EDWARDS J. D., T. A. MOORMANN, *Chem. Met. Eng.*, **24**, 61 (1921).

[2] EDWARDS, J. D., Unpublished Experiments.

[3] PASCAL and JOUNIAUX, *Rev. Metallurgie*, **11**, 1069 (1914).

yolite without dissolved alumina at the same temperature. lcium fluoride, on the other hand, increases the density of uid cryolite. Above the molten metal is a layer of from 6 to inches of molten electrolyte which is essentially a solution of mina (usually about 2 to 5 per cent) in molten cryolite, but lich may also contain other fluorides either added purposely coming from the other metals (*e.g.*, calcium and magnesium) esent in the ash of the anodes. Above the molten electrolyte a crust of solidified electrolyte mixed with aluminum oxide, rough which the anodes project into the electrolyte. In neral, the lower ends of the anodes will be from about 2 to 4 hes from the metal surface.

During operation, the electrolyte is kept in continuous agi- tion by the bubbles of gas (carbon dioxide and carbon onoxide) given off at each anode, and by the effect of the ignetic field produced by the large currents flowing through anode busses, the cell walls, and the lining. Any conductor rrying a current and lying in a magnetic field tends to move in a ection at right angles to this field and to the direction of current, and fused salts are no exception to this rule. Con- juently, the passage of these large currents through the fused ctrolyte from anode to cathode causes a vigorous electro- ignetic stirring of the electrolyte and metal layers, the vigor d direction of the motion being dependent on the current nsity and the distribution and strength of the magnetic d in the cell.

The practical importance of this agitation is seen when we d that the aluminum oxide, which is added to the cell from time time, is actually considerably heavier than either the molten ctrolyte or the molten metal, and if there were no agitation it uld at once sink to the bottom of the cell and accumulate der the metal layer. This would not only prevent the electro- e from dissolving it promptly, but would cause increased istance and overheating at the contact between the metal d the carbon lining. However, if the alumina is fine enough, n though fused alumina with a density of about 4 be used,[1] is maintained in suspension by the agitation of the fused

FRARY, F. C., U. S. Pat. 1,534,031, Apr. 21, 1925; Can. Pat. 256,131; ·. 8, 1925; Br. Pat. 232,189, June 18, 1925; Fr. Pat. 600,146, Nov. 3, :5; Ital. Pat. 238,676, July 8, 1925; Swiss Pat. 115,749, July 1, 1926; rw. Pat. 46,812, Aug. 19, 1929.

electrolyte long enough to permit it to dissolve. The actual time required for 200-mesh alumina to completely dissolve in fused cryolite (2 grams alumina in 150 grams cryolite) has been found by experiment to vary between $1\frac{1}{2}$ and 9 minutes, depending on the temperature, degree of saturation of electrolyte, and the character of the alumina (whether porous, as produced in the Bayer process, or compact, as made by grinding up electrically fused alumina).

It has been proposed, in case fused alumina is used, to mix amorphous (?) alumina from the Bayer process[1] with it. Aluminum carbide may replace all or part of the oxide.[2] It also has been proposed to dissolve the electrothermally fused alumina in a separate crucible of fused cryolite and introduce the completely molten solution into the electrolytic cell.[3]

In the operation of the cell, as the electrolysis continues, the aluminum oxide is used up in direct proportion to the production of metal. As the concentration of the alumina in the fused electrolyte is thus reduced, a point is finally reached when the so-called "anode effect" occurs. The actual concentration of alumina at which this occurs seems to vary somewhat, and probably depends on the temperature and composition of the electrolyte and the anode current density, but in general it is likely to be around 2 per cent. Its occurrence is a signal to the attendant that it is time to add more alumina, which he does by breaking in the crust, on the top of which he had previously distributed a certain amount of alumina. The addition of the alumina and a vigorous stirring of the electrolyte cause the anode effect to disappear and the electrolysis to resume its normal course for several hours, until the electrolyte is again sufficiently impoverished to cause the effect to occur.

There has been considerable discussion of the nature and cause of the anode effect.[4] It manifests itself in a sudden rise in the voltage across the cell, from 6 to 7 volts up to 30 or even 60 volts. In order to detect this change, an incandescent lamp is connected

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[1] HAGLUND, T. R., Fr. Pat. 604,335, May 3, 1926; Swiss Pat. 121,148, June 16, 1927. See also ROCHETTE FRÈRES, Fr. Pat. 511,587, July 29, 1922.

[2] DOLTER, H., Swiss Pat. 119,271, Mar. 16, 1927; Norw. Pat. 44,006, May 9, 1927; Fr. Pat. 609,829, Aug. 25, 1926.

[3] SIEURIN, S. E., Swed. Pat. 54,221, June 6, 1923.

[4] TAYLOR, C. S., *Trans. Am. Electrochem. Soc.*, **47**, 301–316 (1925). ARNDT, K. and H. PROBST, *Z. Elektrochem.*, **29**, 323 (1923).

·oss the terminals of the cell and mounted near it. When ₃ anode effect occurs, the lamp, which had been glowing nly, flashes up and gives a bright light, which attracts the ₎ention of the workman and shows him that it is time to ·ork" the cell.

Careful examination of the cell when the anode effect occurs, ₎ws that the electrolyte no longer "wets" the anodes, as water ts glass, but there is a continuous gaseous envelope covering ₃ whole of the surface of contact between each anode and the ctrolyte, and the current is passing through this envelope as a ₎ltitude of tiny sparks or arcs. The whole of the voltage rease is localized in this gaseous envelope, and the anode face and the gas are, therefore, highly heated. Chemical ₎lysis shows that during the anode effect the gas evolved is ₎e carbon monoxide, whereas at other times it contains from to 90 per cent carbon dioxide. Thus, since a given amount of ₎gen liberated at the anode will produce twice as large a ume of carbon monoxide as of carbon dioxide, and since the ume of a gas is directly proportional to its absolute tempera- ₃, the film of gas represents a very abnormal volume evolved ₎ach anode. Likewise, it represents nearly double the normal bon consumption and five or ten times the normal heat evolu- ₎ and power consumption, so every effort is made to "kill the ₎t" and reëstablish normal conditions as rapidly as possible. The investigations of Arndt[1] and his co-workers show quite ₎rly that we have to do here with a critical anode current ₎sity, which is a function of the alumina concentration (and ₎bably also of temperature and electrolyte composition). As alumina concentration is lowered, the critical current density ₎kewise lowered. When it reaches the actual current density, gas film forms and the voltage rises as above described. ₎bably as the alumina concentration decreases, the anode ₎ential increases, and, consequently, the energy liberated heat) at the anode surface increases. This probably increases proportion of carbon monoxide in the gas, because of the ₎eased speed of reaction between carbon and carbon dioxide higher temperatures. The increased volume of gas evolved ₎eases the area of contact between the anode and the electro- ₃ and, consequently, increases the electrical resistance at the

ARNDT, K. and H. PROBST, *Z. Elektrochem.*, **29**, 323 (1923).
ARNDT, K., *Z. Elektrochem.*, **33**, 236 (1927).

surface of the anode, thus further increasing the evolution of heat and aggravating the condition until the bubbles coalesce into the thin film above described and the anode no longer makes contact at all with the electrolyte. When more alumina has been dissolved and the electrolyte cooled by breaking in the crust, the film fails at some point where the current density is lower than at other points, contact is again reëstablished with the electrolyte, and the film collapses. The anode effect has disappeared as suddenly as it appeared, and normal electrolysis has been resumed.

Since each cell takes a large current at a low voltage, and it is not economical to generate electricity at low voltages, a number of cells are arranged in a "line" or "series,"[1] so that the current passes from each to the next one, and their voltages are added together to make a suitable line or generator voltage. This may be anything between 200 and 600 volts, depending on the power conditions and the design of the plant, so there may be from 30 to 100 cells in a line or series. The line current, supplied by direct-current generators or rotary converters, then passes through all of these cells in series, and anything (such as an anode effect) which affects one cell changes slightly the electrical conditions in all the other cells and the load on the line. Naturally, the effect of such a change in a cell is less, the larger the number of cells in a line. Under normal working conditions, the voltage per cell, including the voltage lost in the busbars and cables connecting it into the circuit, may vary between 5 and 7 volts, depending on the design of the circuit and the cell, age of the cell, state of the electrolyte, anode-cathode distance, and other factors. The power required per pound of aluminum produced also varies, depending on the factors above mentioned and on the care with which the cell is operated. Perhaps 10 to 12 kilowatt hours per pound may be considered normal practice, although some plants will exceed this figure, and some may be able to operate at somewhat less than 10 kilowatt hours per pound. The consumption of carbon anodes varies a great deal, depending on the quality, size, and shape of the anodes and the skill with which the cells are operated. Perhaps 0.6 to 0.8 pound of anodes per pound of aluminum might be considered satisfactory for an efficient plant, although at

[1] HUNT, A. E., U. S. Pat. 582,923, May 18, 1897.
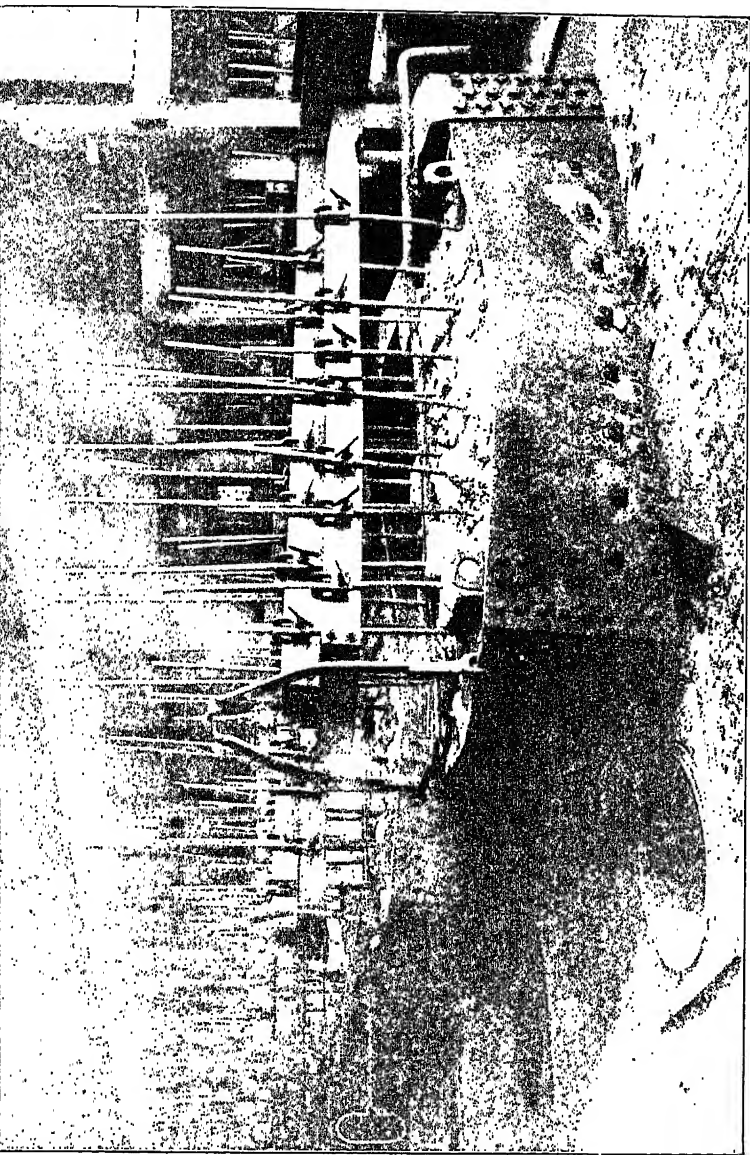
Fig. 60.—Electrolytic cells; cell in stall 2 is beginning to show the anode effect as indicated by glowing electric light seen on post just under Fig. 2; molten electrolyte shows on edge of cell 3.

times some plants will run up to 1 pound of anode per pound of aluminum.

When a sufficient amount of metal has accumulated in the bottom of the cell, it must be removed, either by tapping[1] or ladling. This may be done every day, every second day, or every third day, depending on the design of the cell, the ideas of the management, and local conditions. When the metal is to be tapped out, the tap-hole is opened by driving into it a sharp steel tapping pin, and when enough metal has been removed, it is closed by driving in a wooden plug. From the tapping ladle, the metal is transferred into a larger pouring ladle. The metal from several cells is accumulated in this pouring ladle, then skimmed with a perforated skimmer and poured into molds having a capacity of about 50 pounds each. When the metal is to be ladled out, an anode is removed and a heavy cast-iron cylinder is set into the cell in its place. As the molten electrolyte is now ladled out of the cylinder, the metal rises to take its place, and when it appears it is ladled off into molds. In general, each cast must be analyzed and graded, so that casts may be chosen and mixed in the remelting furnace to produce the grade desired by the customer. Another common practice is to pour the molten aluminum from the tapping or pouring ladles into a "holding furnace." In this way the metal from many cells is blended and finished ingots may be cast from this metal. Practically all commercial aluminum is remelted or heated in holding furnaces to insure uniformity of compositions and the removal of non-metallic impurities.

The electrolytic cell can be started by pouring a suitable amount of molten electrolyte into it, adjusting the anodes, and passing current. Usually, however, molten electrolyte in sufficient quantity is not available and the electrolyte must be fused in place. To do this, the anodes are grounded on the carbon bottom of the cell, and some solid electrolyte shovelled in around them. When current is passed, sufficient heat develops at the point of contact of anode with cathode to gradually fuse the surrounding electrolyte. When a molten layer of sufficient depth has been formed, the anodes are raised, electrolysis commenced, and more electrolyte added until the cell is filled to the proper height.

[1] DICKEY, A., U. S. Pat. 602,575, Apr. 19, 1898.

HALL, C. M., U. S. Pat. 796,325, Aug. 1, 1905.

See also Norw. Pat. 39,159, June 23, 1924.

When a cell is to be removed from service, the electrolyte can be tapped out or, as is more usual, the anodes removed and the cell contents allowed to solidify. It is highly important that the power supply be continuous, for if it is discontinued for many hours, the cell contents will solidify. If power fails, it is sometimes possible to ground the anodes on the bottom of each cell and, later, after the cell contents are frozen, to cautiously increase the current through the cells until the contents are molten again. The process is hazardous, however, because the starting current is irregularly distributed and results in the burning off of anode supports and the expulsion of molten electrolyte from time to time. After a cell is frozen, the contents can be dug out, part of the electrolyte salvaged, and the cell relined for use.

Efficiency of Process.

Many factors affect the efficiency of the reduction process, such as the design of the cell, the operating conditions of current and voltage, and the skill or lack of skill of the workmen caring for the cell. According to Faraday's law, a current of 1,000 amperes, operating at 100 per cent efficiency, will produce about ¾ (0.74) pound of aluminum per hour. In practice the current efficiency varies but is usually between 75 and 90 per cent. The current efficiency is reduced by short circuits, and by reoxidation of reduced metal. Short circuits result from improper adjustment of the carbon anodes which permit contact with the molten aluminum in the bottom of the cell, as well as by current leakage through the crust. Adjustment of the electrodes, and hence current efficiency, may be directly affected by labor conditions. Electrodes also may be temporarily shorted on the carbon bottom during the working of the cell, or current may pass through carbon dust in the frozen crust. The production of aluminum is decreased by reoxidation of the metal after its reduction; this loss of metal decreases the current efficiency of the process. The formation of metal fog or mist is a common phenomenon of electrolytic processes. Metallic aluminum in the form of extremely small particles becomes suspended in the molten electrolyte; this highly dispersed aluminum is known as "metal mist." Because of the circulation of the electrolyte as a result of the electromagnetic forces acting on it, the metal mist is being continually brought into contact

with the carbon anodes, where it may be reoxidized to alumina. The formation of metal mist increases rapidly with increase of temperature above the normal operating range. Hence the current efficiency tends to decrease with increase of electrolyte temperature. The loss of aluminum by reoxidation can be decreased by increasing the distance from the bottom of the anode to the surface of the molten aluminum. This also increases the power consumption, so that the two factors must be nicely balanced in an efficient process.

The exact power efficiency of the process is not known because the voltage required for the electrochemical decomposition of the alumina is known only approximately. Calculations by the methods of thermodynamics indicate values from 0.9 to 2.0 volts for the decomposition voltage, depending on the assumptions made as to the fundamental conditions involved. Experimentally, the decomposition voltage of alumina dissolved in cryolite is very difficult to determine. Estimates of the decomposition voltage, however, made by plotting the current-voltage relation over a wide range of currents indicated potentials of about 1.7 volts. The operating voltage is between 5 and 7 volts; this is several times the decomposition voltage and includes the voltage drop in the molten electrolyte and aluminum, the carbon anode and cathode and connecting members, as well as at all contact surfaces.

Obviously, power, in addition to that required for the electrochemical decomposition of the alumina, is necessary to maintain the electrolyte molten and in mobile condition. The necessary heat is generated by the passage of current through the anodes, electrolyte, aluminum, and cathode. Under steady operating conditions, all the power above that necessary to decompose the alumina must be dissipated as heat. The loss from sides and bottom of the cell can be decreased by suitable insulation as indicated in Fig. 56. This would appear to be advantageous in reducing the power requirements. However, in order to reduce the power input, it is necessary to reduce either the current or the voltage drop in the cell. If the current is reduced, the production of aluminum is correspondingly diminished. If the anode-cathode distance is decreased by setting the anodes lower, the voltage drop in the electrolyte is lowered and the heat generated in the electrolyte is also lowered. With a lower temperature at the surface of the aluminum, the tendency for
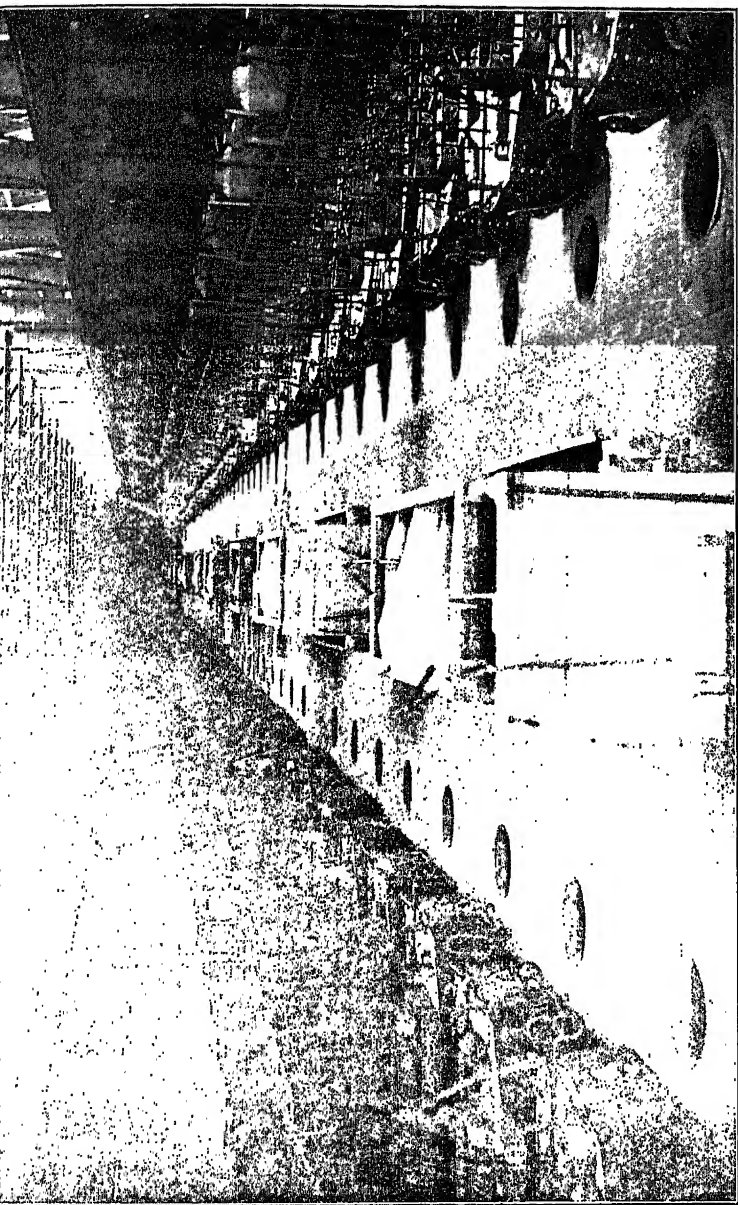
Fig. 61.—Electrolytic cell room.

aluminum to form a metal mist is lessened, but with the decreased añode-cathode distance the loss by reoxidation is increased. Also, with lower cell temperatures, the loss of carbon from the anodes by oxidation in the air is diminished, which is a desirable result.   Consequently, in the design and operation of a cell, a nice balance must be struck between current, voltage, anode area, anode-cathode distance, thermal insulation, etc., in order to produce aluminum at the lowest cost per pound.   This is the result aimed at, rather than to secure the greatest electrical or thermal efficiency.

Other Electrolytic Processes.

Although the only process in use for the production of pure aluminum is based on the electrolysis of alumina dissolved in cryolite, other electrolytes have been tried or suggested.   The electrolysis of the double chloride of aluminum and sodium ($NaCl.AlCl_3$) was first tried by Bunsen and Sainte-Claire Deville; on a commercial scale it failed, in part because of the volatility and instability of the electrolyte.   It also had to be operated below the melting point of aluminum.   The electrolysis of cryolite was attempted and was found impractical, if for no other reason than that the anode effect was almost continuous; this necessitated a high potential for electrolysis.   Mixtures of sodium-aluminum chloride with cryolite, and also of aluminum fluoride and sodium chloride were tried and found wanting. Proposals have even been made to electrolyze aluminum chloride in a closed cell.

A comparison of the heats of formation of aluminum oxide and aluminum sulfide shows that of aluminum sulfide to be substantially lower and indicates that its decomposition voltage would be lower than that of the oxide.   If this is so, less power would be required to produce aluminum from the sulfide than from the oxide, other conditions being equal.   Certain disadvantages are at once apparent, as for example, the fact that aluminum sulfide reacts with moist air to form the very poisonous gas, hydrogen sulfide.   No practical process with the sulfide has been developed.

Bucherer[1] proposed to dissolve sodium aluminum sulfide ($Na_6Al_2S_6$) in an electrolyte of alkali or alkaline earth fluorides

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[1] Bucherer, A., Ger. Pat. 63,995, July 27, 1892.

or chlorides and electrolyze. The next suggestion[1] was to use aluminum sulfide instead of sodium aluminum sulfide. Blackmore[2] proposed to use a molten electrolyte of sodium and potassium sulfide with alkali thiocarbonates, while Gin[3] suggested an electrolyte composed of aluminum fluoride and sodium sulfide. Keogh[4] starts with fused sodium chloride to which is added anhydrous aluminum sulfate and carbon. The hope is that the sulfate will be reduced to sulfide by the carbon and that aluminum sulfide will be formed which can then be reduced to metallic aluminum by electrolysis of the mixture. Kissock[5] thinks that alumina should be converted to aluminum carbide in the electric furnace and then heated with sulfur or a sulfide to convert it to aluminum sulfide. This compound is then "dissolved and electrolyzed in a molten bath of alkaline earth chlorides or fluorides." These sulfide processes are of passing historical interest only and represent hopes rather than probabilities.

ELECTRICAL EQUIPMENT FOR REDUCTION PLANTS

As has been stated, the reduction of aluminum from its oxide requires direct currents of large volume, but the individual electrolytic cells each consume only 5 to 7 volts. Consequently, for economical operation, it is necessary to arrange a number of these cells in series. Practice in this respect varies somewhat, but in general the generator voltage will lie between 200 and 600 volts, and each line of cells will take from 8,000 to as much as 30,000 amperes.

In some works each line of cells is supplied with power from a direct-current generator which is directly driven by a water wheel or other prime mover, while in other cases such generators may be connected in parallel on a bus system from which the lines of cells are operated. Such an arrangement is, of course, only feasible where the electrolytic plant is located at the water power or steam plant. In general, most water powers are not conveniently located with reference to a suitable site for construction of a reduction plant, together with the necessary carbon

[1] ALUMINIUM INDUSTRIE, A.-G., Ger. Pat. 68,909, May 1, 1893.

[2] BLACKMORE, H. S., U. S. Pat. 605,380, June 7, 1898.

[3] GIN, G., U. S. Pat. 763,479, June 28, 1904; Ger. Pat. 148,627, Jan. 29, 1904; Swed. Pat. 16,675, Nov. 21, 1903; Norw. Pat. 12,397, Nov. 23, 1903.

[4] KEOGH, L. R., U. S. Pat. 996,094, June 27, 1911.

[5] KISSOCK, A., U. S. Pat. 1,052,727, Feb. 11, 1913.

plant, townsite, etc. Frequently, also, the reduction plant
uses only a part of the power generated by the hydro-electric
plant. Consequently, the more common arrangement, at least
in the larger plants, is to generate alternating current at a suitable
voltage in the hydro-electric plant, transform it to a higher
voltage if necessary for transmission to any considerable distance,
and transmit it to the reduction plant, where it passes through
transformers that reduce the voltage to the proper point for the

Fig. 62.--Rotary converter station for supplying direct current to cells.

rotary converters. These machines rotate in synchronism with
the generators in the hydro-electric plant and convert the
alternating current into direct current. The lines of cells may
be so arranged that each rotary converter or group of rotary
converters feeds one line of cells, or a number of rotary con-
verters may be operated in parallel on a bus system and the
lines of cells likewise operated in parallel from the bus system.
The latter arrangement is considerably more flexible from an
operating standpoint, since it permits the shutting down of any

machine at any time for inspection and repairs, without interfering with the operation of the reduction plant.   ·

THE REFINING OF ALUMINUM

The Hall process, in ordinary operation, seldom produces metal having a purity higher than about 99.7 per cent. The impurities come mainly from the electrolyte, the alumina, and the carbon anodes. By special attention to the operation of the cells and by careful addition of only the purest materials, it has been possible to produce aluminum having a slightly higher purity than 99.7. However, a practical method of taking impure aluminum and eliminating the impurities by a refining process in order to produce aluminum of high purity has many interesting possibilities. A proposal to refine aluminum electrolytically, using a fused salt electrolyte, was first made by William Hoopes about 1900, and his proposal was tried out in modified form and on a small scale by Charles M. Hall, using the arrangement shown in Hoopes' U. S. patent 673,364, of April 30th, 1901.[1] Mr. Hoopes' original proposition, however, as made to Mr. Hall, was to use a refining cell with three liquid layers, in which a molten aluminum cathode would float on an electrolyte heavier than molten aluminum instead of on cryolite, which is lighter than aluminum; the anode alloy would be still heavier than the electrolyte and would lie on the bottom of the cell. Such an arrangement was later proposed independently by Betts.[2]

The electrolyte preferred by Betts was cryolite saturated with alumina, or a mixture of cryolite and barium chloride; the anode might be aluminum alloyed with iron, copper, zinc, or other heavy metals, and might be either liquid or solid. Unfortunately, experiment shows that the addition of alumina to cryolite reduces its specific gravity in the molten state, instead of increasing it, so molten aluminum would not float on such an electrolyte. Also, barium chloride has been proved to be poorly adapted as an addition agent for many reasons, especially because the presence of a chloride causes large loss by volatilization, and also weakens the selective activity of the

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[1] Also, Br. Pat. 8,153, May 25, 1901; Ger. Pat. 133,909, Sept. 20, 1902.

[2] BETTS, A. G., U. S. Pat. 795,886, Aug. 1, 1905; Br. Pat. 7,277 (1906); Ger. Pat. 186,182, June 12, 1907; Norw. Pat. 16,723, Aug. 26, 1907; Fr. Pat. 364,521, Aug. 23, 1906.

electrolyte, so that too much iron and silicon are dissolved from the anode and carried over to the cathode.

A more recent patent to Tucker[1] revives the proposal of using a cryolite electrolyte leaving both anode and cathode layers on the bottom of the cell, separated and insulated by a wall of frozen bath. The irregular current distribution and the concentration of power (and heat) on the surface of the dividing wall would probably make it impossible to keep such a cell in practical operation for any length of time. The voltage requirement also would be much larger than for a cell of the three-liquid-layer type, where anode and cathode surfaces are parallel and may be only a few inches apart over the whole area.

It has also been proposed to operate an electrolytic refining process with solid anode and cathode, using the low-melting (but volatile!) double chloride of sodium and aluminum as the electrolyte and an aluminum-iron-silicon anode.[2]

A method of purifying aluminum has been patented[3] which depends upon the partial melting of the aluminum. The impurities, iron in particular, are said to concentrate in the mother liquor as low-melting eutectics and may be separated from the aluminum by pressing the liquid from the solid metal.

Hoopes Refining Process.

About 1919, Wm. Hoopes, with the coöperation of the research staff of Aluminum Company of America, developed a commercial cell and process for the electrolytic refining of aluminum, using the three-liquid-layer cell which he had originally proposed.[4] In Fig. 63 is shown a cross-section of the new Hoopes cell for the electrolytic refining of aluminum.[5] The cell itself is divided

[1] Tucker, S. A., U. S. Pat. 1,384,499, July 12, 1921.

[2] Aluminium Industrie, A.-G., U. S. Pat. 1,709,759, Apr. 16, 1929; Argentine Pat. 27,552, Aug. 1, 1927; Fr. Pats. 635,541, Mar. 17, 1928; 638,465, May 25, 1928; 642,550, Aug. 30, 1928; 642,664, Sept. 1, 1928; Swiss Pat. 128,513, Nov. 1, 1928; Br. Pats. 265,170; 305,458, Apr. 4, 1929; Sp. Pat. 100,929, Dec. 31, 1926.

[3] Physikalisch-Technische Reichsanstalt, Ger. Pat. 326,160, Sept. 23, 1920.

[4] Frary, F. C., "Electrolytic Refining of Aluminum," *Trans. Am. Electrochem. Soc.*, **47**, 1 (1925).

[5] Hoopes, Wm., U. S. Pat. 1,534,320, Apr. 21, 1925; Can. Pat. 256,122, Dec. 8, 1925; Br. Pat. 208,710, Feb. 26, 1925; Austral. Pat. 15,706/23, July 3, 1924; Braz. Pat. 15,407, May 4, 1926; Czecho-Slov. Pat. 25,413, Apr. 9, 1928; Hung. Pat. 87,090, Oct. 9, 1924; Ital. Pat. 226,712, Feb. 8, 1924; Jap. Pat. 61,343, Oct. 6, 1924; Jugo-Slav. Pat. 3,291, Dec. 1, 1925; Mex. Pat. 23,346, Dec. 28, 1923.

into two electrically insulated sections, arranged with water cooling at the joints to aid in maintaining the electrical insulation between the sections. This is quite essential in order to prevent partial short circuits between the anode and cathode through the hot lining. The lower half of the cell contains a carbon
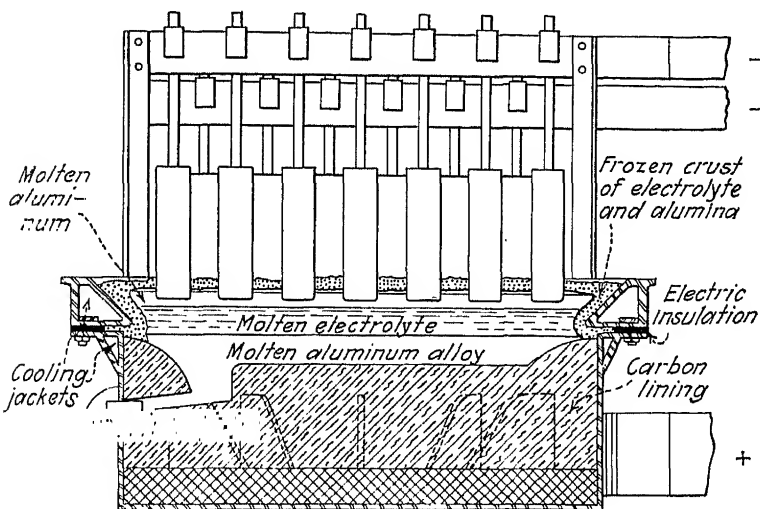
FIG. 63.—Diagram of electrolytic refining cell.

bottom lining, on which rests the molten anode alloy. Superimposed upon this is the molten electrolyte, and upon this floats the molten cathode.

The electrolyte is composed of a mixture of cryolite, aluminum fluoride, and barium fluoride, nearly saturated with alumina.[1]

[1] HOOPES, WM., F. C. FRARY, J. D. EDWARDS, U. S. Pat. 1,534,318, Apr. 21, 1925; Can. Pat. 256,125, Dec. 8, 1925; Br. Pat. 208,713, Mar. 13, 1925; Fr. Pat. 575,465, Apr. 23, 1924; Norw. Pat. 43,439, Nov. 22, 1926; Austral. Pat. 15,707/23, May 19, 1924; Aust. Pat. 106,695, June 25, 1927; Belg. Pat. 314,427, Dec. 31, 1923; Braz. Pat. 14,736, Jan., 1925; Br. Guiana 183, Apr. 10, 1924; Chil. Pat. 5,483, June 25, 1925; Czecho-Slov. 19,437, June 23, 1926; Holland Pat. 18,588; Swiss Pat. 109,527, Apr. 1, 1925; Venezuela Pat. 689, Jan. 21, 1924; Hung. Pat. 88,544, May 18, 1925; India Pat. 9,922, Dec. 20, 1923; Ital. Pat. 226,714, Feb. 8, 1924; Jap. Pat. 61,345, Oct. 6, 1924; Jugo-Slav. Pat. 3,293, Dec. 1, 1925; Mex. Pat. 23,349, Dec. 28, 1923; Portug. Pat. 13,516, Dec. 11, 1924; Roum. Pat. 8,916, Dec. 18, 1923; S. Afr. Pat. 1,228/23, Dec. 20, 1923; Span. Pat. 87,753, Mar. 12, 1924.

A suitable electrolyte may have the following approximate composition:

Barium fluoride	30 to 38 per cent
Sodium fluoride	25 to 30 per cent
Aluminum fluoride	30 to 38 per cent
Alumina	0.5 to 7 per cent
Calcium and magnesium fluorides (present as unavoidable impurities)	about 2 per cent

The density of aluminum (99.75 per cent purity) at 1000°C. is 2.29 grams per cubic centimeter. At this temperature, molten cryolite has a density of only 2.10 grams per cubic centimeter, and in order to increase its density so that molten aluminum will float on it at that temperature it is necessary to add about 20 parts of barium fluoride to each 80 parts of cryolite. Mixtures of cryolite containing between 20 and 60 per cent of barium fluoride are satisfactory and have densities ranging between 2.38 and 3.15 grams per cubic centimeter at 1000°C. Strontium fluoride can replace the barium fluoride to a certain extent, but calcium fluoride is much less effective in increasing the density and in other respects. An electrolyte containing aluminum fluoride in excess of that required to form cryolite with the sodium fluoride present is to be preferred, since it minimizes the production of sodium at the cathode. The density of these molten electrolytes decreases more rapidly with rising temperature than does the density of the molten aluminum cathode. It is desirable, therefore, to maintain sufficient margin between the two densities, so that if the cell becomes overheated the electrolyte will not become so light as to permit the top layer to sink through the electrolyte. The density of electrolyte of the approximate composition given above is about 2.5 to 2.7 grams per cubic centimeter at 950°C., and 2.4 to 2.6 at 1100°C. Pure aluminum has a density of about 2.30 at 950°C. and 2.26 at 1100°C., so that it will readily float on the electrolyte at these temperatures.

By virtue of the cooling effect of the side walls of the cell, there is built up on these walls by a process of selective crystallization, a thick crust very rich in alumina, which is very refractory and not easily dissolved away by the electrolyte if for any reason the temperature of the cell rises above normal.[1] This crust

[1] HOOPES, W., B. T. HORSFIELD, J. D. EDWARDS, U. S. Pat. 1,534,322, Apr. 21, 1925; Can. Pat. 256,124, Dec. 8, 1925; Br. Pat. 208,712, Mar. 12, 1925; Ger. Pat. 465,336, Oct. 1, 1928; Fr. Pat. 575,466, Apr. 23, 1924;

serves electrically and thermally to insulate the molten electrolyte from the shell; it also minimizes the leakage of current from anode to cathode through the walls. It is very important in starting up such a cell, to make sure that the upper half is maintained in an electrically neutral condition, in order to prevent the formation of a side crust partially contaminated with metal. Such a crust seems to conduct enough current to cause electrolysis to take place in it, and its content of metal gradually increases until its conductivity becomes prohibitively high.

Graphite electrodes dipping into the floating aluminum layer are used in order to make the electrical connection to the molten cathode.[1] These are carried on heavy copper rods, as shown in the figure. By maintaining the proper conditions, a crust of frozen bath rich in alumina can be caused to form over the upper surface of the metal and around the electrodes and act as a protective cover. Care must be taken to maintain an adequate metal thickness in the cathode layer; otherwise, the heavy currents and powerful magnetic fields set up a swirling motion so violent that anode and cathode layers can come in contact in spots. This, of course, results in their union and the loss of the refined metal.

There seems to be only one practical anode for such a cell. This is a copper-aluminum alloy, low in iron and titanium (which raise its freezing point) and preferably containing enough silicon to lower its freezing point considerably, so that it will remain adequately mobile even when the aluminum content has been largely reduced.[2] Of course, the composition, and hence

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Norw. Pat. 43,441, Nov. 22, 1926; S. Afr. Pat. 1,231/23, Apr. 19, 1924; Span. Pat. 87,752, Mar. 12, 1924; Swed. Pat. 64,909, Dec. 20, 1923; Swiss Pat. 109,528, Apr. 1, 1925; Venez. Pat. 690, Jan. 21, 1924.

[1] FRARY, F. C., U. S. Pat. 1,535,458, Apr. 28, 1925; Can. Pat. 256,129, Dec. 8, 1925; Br. Pat. 224,488, Jan. 22, 1925.

[2] HOOPES, W., F. C. FRARY, J. D. EDWARDS, U. S. Pat. 1,534,317, Apr. 21, 1925; Can. Pat. 256,127, Dec. 8, 1925; Br. Pat. 208,715, Apr. 20, 1925; Austral. Pat. 15,709/23, May 19, 1924; Braz. Pat. 15,129, Oct. 3, 1925; Czecho-Slov. Pat. 21,158, Jan. 12, 1927; Hung. Pat. 88,742, June 19, 1925; Ital. Pat. 226,693, Feb. 15, 1924; Jap. Pat. 61,347, Oct. 6, 1924; Jugo-Slav. Pat. 3,292, Dec. 1, 1925; Mex. Pat. 23,345, Dec. 28, 1923; Fr. Pat. 575,463, Apr. 23, 1924; Norw. Pat. 43,440, Nov. 22, 1926; Aust. Pat. 106,694, Apr. 25, 1927; Belg. Pat. 314,426, Dec. 31, 1923; Br. Guiana Pat. 182, Apr. 10, 1924; Chil. Pat. 5,482, June 25, 1925; Holland Pat. 18,589; India Pat. 9,924/23 June 4, 1925; Portug. Pat. 13,514, Dec. 11, 1924; Roum. Pat. 8,915, Dec. 18, 1923; S. Afr. Pat. 1,230/23, Apr. 19, 1924; Span. Pat. 87,751, Mar. 12, 1924.

the density, of the anode alloy changes continuously as the refining process proceeds. An alloy of aluminum and copper with only about 25 per cent copper has a density of about 2.8 at 950°C., which is sufficiently high to insure that the alloy will not float but will remain beneath the electrolyte; the density increases as the copper content is increased by the removal of the aluminum.

It has recently been proposed to use an anode alloy of aluminum with gold, silver, or platinum as the heavy alloying metal.[1] The advantage claimed is that a lower concentration of gold or platinum, for example, is required to give the anode alloy the density necessary to keep it at the bottom of the cell and, hence, there is less chance of contaminating the pure aluminum cathode; the disadvantages are obvious!

The proper working temperature of the Hoopes cell is limited by the properties of the fused electrolyte, and lies between about 900 and 1100°C. In the nature of things, the anode alloy tends to be cooler than the electrolyte. If any appreciable amount of it freezes, copper and other impurities will be dissolved from the frozen portions by the current, and the refined metal will be contaminated. It is quite essential, therefore, to maintain the mobility of the anode alloy.

The cell is easily started by pouring into it a layer of molten electrolyte several inches thick, lowering the graphite connectors to dip into the electrolyte layer, and turning on full-load current. A layer of molten anode alloy is then slowly poured in, taking care that the joint between the upper and lower halves of the cell is covered only by the electrolyte. A layer of molten aluminum carefully poured onto the surface of the electrolyte, followed by a final adjustment of the graphite connectors, completes the operation, and if the electrolyte is of proper composition the alumina-rich side crust and top crust will soon begin to form, and in a few hours the cell is in normal operation.

In order to keep the cell operating continuously, the aluminum produced at the cathode must be tapped off, and a corresponding amount of impure aluminum or aluminum-copper alloy added to the anode from time to time. If the cell is being used to refine impure aluminum, this operation may be carried out

[1] DEUT. VERSUCH. F. LUFTFAHRT, Br. Pat. 276,911, Sept. 8, 1927; Fr. Pat. 639,173, June 15, 1928; Ger. Pat. 454,646, Jan. 13, 1928; Swiss Pat. 128,047, Oct. 1, 1928; Norw. Pat. 45,418, July 30, 1928.

simply in two steps. The necessary amount of the molten impure aluminum is poured into a suitable crucible, which is placed in a hole in the floor in front of the anode-alloy tap hole. The current is then cut off, the tap hole opened, and a few hundred pounds of the impoverished anode alloy tapped into the crucible of molten aluminum, so as to produce an alloy heavier than the molten electrolyte. This alloy is then poured back into the cell through a suitable carbon-lined funnel, extending into the anode-alloy layer. As the level of the molten mass in the cell rises, the tapping trough[1] in the top section is opened, and the pure cathode metal is allowed to flow out into another crucible, the amount obtained being, of course, approximately the same as that of the new aluminum added.

The cells operate with excellent current efficiency, on from about 5 to 7 volts and about 20,000 amperes, and require little attention except at tapping time. A certain amount of sodium is produced at the cathode, and together with some of the aluminum, is gradually oxidized. This results in a gradual thickening of the side crust, and from time to time the excess of alumina is removed by digging out some of this side crust and adding fresh electrolyte. The cells have been operated continuously for long periods under works conditions, and it has been shown to be entirely practical thus to produce any desired amount of metal with an average purity of over 99.80 per cent. In fact, much of the metal will be 99.90 per cent pure, and some metal as pure as 99.99 per cent has been produced.

ELECTROTHERMAL PRODUCTION OF ALUMINUM AND ALUMINUM ALLOYS

The practical difficulties in the way of producing aluminum by electrothermal reduction of alumina with carbon have already been touched upon briefly. Not only is the required temperature very high, but it is also very near the boiling point of aluminum. As a result, the aluminum is quite volatile and difficult to retain in the furnace. Also, because of the high temperature, the volume of gas produced is very large (at 2000°C. it would be about 170 cubic feet per pound of aluminum) and this fact further complicates the problem of recovering the aluminum.

In order to estimate the temperature at which carbon will reduce alumina some interesting calculations with regard to the

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[1] HOOPES, WM., U. S. Pat. 1,562,090, Nov. 17, 1925.

equilibrium relationships between alumina, carbon and carbon monoxide have been made by C. S. Taylor. In making these calculations, the heat of formation of aluminum oxide has been taken as 378,000 calories, which is an average of the results of Berthelot,[1] and those of Parr and Moose.[2] The heat of formation of carbon monoxide, as given by Lewis and Randall[3] also has been employed.

$$Al_2O_3 = 2Al + 3O \qquad \Delta H_{298} = 378,000; \Delta F^\circ{}_{298} = 356,300. \quad (1)$$
$$3C + 3O = 3CO \qquad \Delta H_{298} = -78,450; \Delta F^\circ{}_{298} = -97,530. \quad (2)$$
$$Al_2O_3 + 3C = 2Al + 3CO \; \Delta H_{298} = 299,550; \Delta F^\circ{}_{298} = 258,770. \quad (3)$$
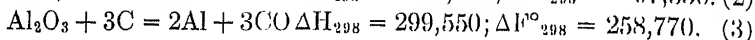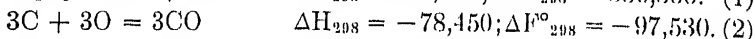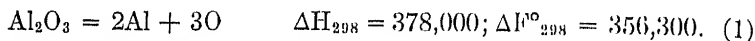
Combining the appropriate heats of reaction and free energy for the first two equations gives, for the heat of reduction of alumina by carbon, the value (ΔH_{298}), 299,550 calories, and for the change in free energy ($\Delta F^\circ{}_{298}$), 258,770 calories. Using the best obtainable values for the specific heats of the elements and compounds concerned, and making allowance for the latent heat of fusion of aluminum, Taylor has calculated (by the methods of Lewis and Randall) the equilibrium constant for the reaction ($K = p^3{}_{co}$) as $\mathrm{Log}\ K = 30.22 - \dfrac{65544}{T}$. From this equation the partial pressure of carbon monoxide in equilibrium with alumina and carbon at various temperatures can be readily calculated and the values for temperatures from 1500 to 2000°C. are given in Table 6.

These values permit an estimate of the lowest temperature at which alumina can be reduced to aluminum by carbon at atmospheric pressure. This minimum reaction temperature would be the temperature at which the sum of the partial pressure of the carbon monoxide and the partial pressure of aluminum vapor from the reduced aluminum would be equal to 1 atmosphere. Assuming the boiling point of aluminum to be 1800°C., according to the observations of Greenwood,[4] and using the values for the vapor pressure of aluminum calculated by Millar,[5] it is found that at about 1750°C. the sum of the partial pressures of carbon monoxide (240 millimeters) and aluminum (520

[1] Berthelot, *Ann. chim. phys.*, (7) **22**, 482 (1908).

[2] Parr, S. W. and J. E. Moose, *J. Am. Chem. Soc.*, **46**, 2656 (1924).

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York (1923).

[4] Greenwood, *Proc. Roy. Soc.* (London) **A83**, 483 (1910).

[5] Millar, R. W., *Ind. Eng. Chem.*, **17**, 34 (1925).

millimeters) equaled one atmosphere. This, of course, is a minimum reaction temperature, and a higher temperature would have to be reached before the rate of reduction would be appreciable. Practical experience shows that a temperature of at least 1800°C. or higher has to be employed, and theory and practice in this case seem to be in substantial agreement. Although thermodynamic considerations lead to interesting conclusions regarding equilibrium relations, they give no information as to the rate at which the reaction will proceed.

TABLE 6.—PRESSURE OF CARBON MONOXIDE IN EQUILIBRIUM WITH ALUMINA AND CARBON AT VARIOUS TEMPERATURES

$$Al_2O_3 + 3C = 2Al + 3CO$$
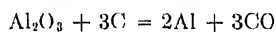
$$\left(Log \ p_{co} \text{ (in atmospheres) } = 10.074 - \frac{21848}{T} \right)$$

Temperature, degrees Centigrade	Partial pressure of carbon monoxide in equilibrium	
	Pressure, atmospheres	Pressure, millimeters
1500	5.64×10^{-3}	4
1600	2.56×10^{-2}	20
1700	0.100	76
1800	0.343	261
1896	1.000	760
2000	2.897	2,200

Although the equations indicate that under reduced pressure of carbon monoxide, the reaction will proceed at a lower temperature, it is doubtful in practice whether any such result could be obtained. With a view to preventing the reoxidation of aluminum by carbon monoxide, various inventors[1] have suggested carrying out the reaction in a vacuum, or at least under reduced pressure. This, however, would be exceedingly difficult to do on a commercial scale at the necessary temperatures. On the other hand, a patent to Burgess[2] recommends carrying out the reduction in a closed chamber under pressure!

[1] GIULINI, G., U. S. Pat. 1,257,995, Mar. 5, 1918; Br. Pat. 8166 (1913) Jan. 29, 1914; Aust. Pat. 69,179, June 25, 1915; Norw. Pat. 27,306, Oct. 9, 1916.

[2] BURGESS, L., U. S. Pat. 1,512,271, Oct. 21, 1924.

The production of aluminum by the reduction of alumina with carbon is always complicated by the formation of aluminum carbide according to the reaction,

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO.$$
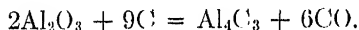
The equilibrium conditions for this reaction have been investigated by Prescott and Hincke.[1]   These investigators found that the equilibrium pressure of carbon monoxide is 1 atmosphere at 1978°C.   Frary[2] has described the difficulties experienced in electric furnace operation when an excess of aluminum carbide or alumina accumulates in the furnace.   To secure regular operation, the dross floating on the alloy in the furnace is tested to determine whether aluminum carbide or alumina is in excess. Alumina may then be added to the furnace to reduce the excess carbide, or coke may be added to reduce excess alumina.

Although no one has devised a practical scheme for recovering pure aluminum from the reduction products of alumina and carbon, nevertheless its recovery in the form of an aluminum alloy is well known and practical.   E. H. and A. H. Cowles were the first to accomplish this, and as early as 1885 they mixed corundum with granulated carbon and metallic copper and, by the passage of electric current through the charge, heated it to the reduction point and produced an aluminum-copper alloy. They were able to make alloys containing as high as 40 per cent aluminum, although it was much easier and more practical to make an alloy containing about 30 per cent or less of aluminum.

Copper is substantially less volatile than aluminum   its boiling point is 2300°C. as compared with about 1800°C. for aluminum— and, hence, can be used to absorb the metallic vapor of aluminum as it is produced.   The partial pressure of the aluminum in an alloy is very much lower than that of pure aluminum at the same temperature.   The aluminum can thus be conveniently recovered by absorption in a less volatile metal. Silicon (boiling point = 2600°C.)[3] and iron (boiling point = 3000°C.)[3] are even less volatile than copper and can be used to collect the reduced aluminum.   Somewhat higher concentrations of aluminum can be obtained in the aluminum-silicon and

[1] PRESCOTT, JR., C. H., W. B. HINCKE, *J. Am. Chem. Soc.*, **49**, 2753 (1927).

[2] FRARY, F. C., U. S. Pat. 1,594,362, Aug. 3, 1926.

[3] International Critical Tables.

aluminum-iron alloys than with the aluminum-copper alloys because of the lower volatility of the silicon and iron. Aluminum alloys containing as high as 75 per cent aluminum have been made by electrothermal reduction, but not on a commercial scale. When an attempt is made to attain a high concentration of aluminum in the reduced alloy, it is necessary to use a larger quantity of carbon in the charge and there is a greater tendency for the reduced alloy to be contaminated with carbides. The higher the content of aluminum or silicon in the alloy, the lighter is the alloy and the greater the difficulty of separating it from any slag which may be produced in the smelting operation.

Since 1920 an extensive use of aluminum-silicon alloys has been developed and considerable interest has been shown in the electrothermal production of these alloys. It is stated that by keeping the silicon content above 35 per cent, or preferably around 40 per cent, an aluminum-silicon alloy can be electrothermally produced from a mixture of alumina and silica without appreciable contamination by carbides.[1] Another Swiss patent[2] suggests that carbides can be separated from the electrothermally produced aluminum-silicon alloy by slow cooling of the alloy, followed by casting it in molds. A Swiss patent refers to the smelting of a briquetted mixture of kaolin, petroleum coke, and tar in order to produce an aluminum-silicon alloy.[3] The obvious claim is made that if an iron-free alloy is desired, the raw materials of the charge should be correspondingly free of iron. Electrothermally produced aluminum-silicon alloys have been made and sold commercially for some time.

A variety of ideas with regard to the electrothermal production of aluminum and aluminum alloys have been patented. After the pioneer development of the Cowles brothers, Willson[1] described the production of aluminum alloys by striking an electric arc between a carbon electrode and a copper electrode in the presence of a mixture of alumina and carbon. Willson[5] also recommended impregnating the alumina with tar or other reducing agent to secure an intimate mixture of the two before heating to the reducing temperature. A similar proposition,

[1] ELEKTRIZITÄTSWERK LONZA, Swiss Pat. 121,605, July 1, 1927.

[2] ELEKTRIZITÄTSWERK LONZA, Swiss Pat. 125,273, Apr. 2, 1928.

[3] ALUMINIUM INDUSTRIE, A.-G., Swiss Pat. 102,796, Jan. 2, 1924.

[4] WILLSON, T. L., U. S. Pat. 491,394, Feb. 7, 1893; Br. Pat. 21,701 (1892) Sept. 30, 1893.

[5] WILLSON, T. L., Br. Pat. 21,696 (1892) Sept. 30, 1893.

although patented much later, is that of Burgess,[1] who mixes alumina with tar, pitch, asphalt, etc., and cokes the mixture in order to secure intimate contact between alumina and carbon. Lime[2] is one such addition agent which is said to act beneficially as a flux; the claim is also made that it forms calcium carbide which acts as a reducing agent on Al_2O_3. Serpek[3] states that the addition of strontium or barium compounds largely prevents volatilization of aluminum from the furnace; he claims to obtain a mixture of aluminum and aluminum carbide. Another proposal[4] is to produce electrothermally an aluminum-silicon-iron alloy and then separate the aluminum by fractional distillation under reduced pressure. The distillation of an alloy containing 45 per cent aluminum, 50 per cent silicon, and 5 per cent iron is mentioned specifically. The reduction would be carried out in one chamber of the furnace, and the reduced alloy would then flow into an adjacent chamber where the distillation of the aluminum would occur.

Onda[5] reduces a mixture of carbon, alumina (bauxite), and a metallic sulfide with the formation of a molten slag containing aluminum sulfide, and with the recovery of an aluminum alloy. Along the same lines, Haglund[6] has recommended the use of a a sulfide-containing slag in the electrothermal production of aluminum in order to minimize the volatilization of aluminum. The slag, of course, must be considerably lighter than the alloy in order to permit satisfactory separation of the two. In an earlier patent, Peniakoff[7] expressed the idea that aluminum sulfide could be reduced by carbon monoxide, carbon, or a hydrocarbon gas. Tone[8] has recommended carrying out the reduction in two steps, first reducing alumina to aluminum

[1] BURGESS, L., U. S. Pat. 1,379,523, May 24, 1921; Br. Pat. 182,609, July 13, 1922; Fr. Pat. 535,084, Apr. 8, 1922; Can. Pat. 218,326.

[2] RHEINISCHE ELEKTROWERKE, A.-G., Ger. Pat. 308,542, July 29, 1920; DE SOUZA, A. E., Fr. Pat. 353,277, Sept. 7, 1905

[3] SERPEK, O., Ger. Pat. 206,588, Feb. 9, 1909; Swiss Pat. 42,567, Mar. 14, 1908.

[4] ALUMINIUM INDUSTRIE, A.-G., Swiss Pats. 121,147, June 16, 1927; 121,604, Aug. 1, 1927; Ger. Pats. 456,806, Mar. 2, 1928; 466,551, Oct. 9, 1928.

[5] ONDA, M., U. S. Pat. 760,554, Mar. 4, 1904.

[6] HAGLUND, T. R., U. S. Pat. 1,512,462, Oct. 21, 1924; Can. Pat. 251,381, July 7, 1925; Fr. Pat. 567,481, Mar. 3, 1924; Ger. Pat. 107,927, Jan. 3, 1925; Norw. Pat. 37,980, Oct. 1, 1923.

[7] PENIAKOFF, A., Ger. Pat. 83,638, Oct. 17, 1895.

[8] TONE, F. J., U. S. Pat. 961,913, June 21, 1901.

carbide, and then, by reaction with more alumina, producing metallic aluminum. It is Tone's idea that the production of aluminum would be facilitated because less gas (carbon monoxide) would be liberated in the second-stage reduction of aluminum carbide. Askenasy[1] makes the statement that, "If ·aluminum carbide be heated in a crucible in an ordinary metal smelting furnace, say somewhat above the melting point of aluminum, experience has demonstrated that the aluminum gushes from the carbide like water from a sponge." It was his idea that somewhere not far above the melting point of aluminum there was a critical temperature at which aluminum carbide would spontaneously decompose with the formation of metallic aluminum. This behavior, however, has not been verified, nor does it sound at all probable.

Pure Aluminum from Electrothermally Produced Alloy.

Although only alloys of aluminum have been ·practically produced by electrothermal reduction of alumina, nevertheless it is possible by electrolytically refining the alloy to produce pure aluminum from it. The combination of the electrothermal reduction process with the electrolytic refining process thus offers a means of producing pure aluminum from impure materials without the necessity of producing a very pure alumina such as is required for the electrolytic reduction process. William Hoopes, working with the research staff of Aluminum Company of America, has developed such a combination process and tried it out on a substantial scale.[2]

Aluminum alloys with either iron, silicon, or copper can be readily produced by electrothermal reduction. Only the aluminum-copper alloy, however, can be satisfactorily used for electrolytic refining. It is essential in the electrolytic refining

[1] ASKENASY, PAUL, Br. Pat. 23,315 (1909), Void.

[2] HOOPES, WM., F. C. FRARY, J. D. EDWARDS, U. S. Pat. 1,534,316, Apr. 21, 1925; Can. Pat. 256,128, Dec. 8, 1925; Br. Pat. 208,716, Apr. 20, 1925; Austral. Pat. 15,710/23, Jan. 27, 1924; Braz. Pat. 14,737, Jan. 1925; Czecho-Slov. Pat. 24,721, Feb. 1, 1928; Hung. Pat. 88,543, May 18, 1925; India Pat. 9923, Dec. 20, 1923; Ital. Pat. 226,715, Feb. 8, 1924; Jap. Pat. 61,348, Oct. 6, 1924; Jugo-Slav. Pat. 3295, Dec. 1, 1925; Mex. Pat. 23,348, Dec. 28, 1923; Fr. Pat. 575,464, Apr. 23, 1924; Norw. Pat. 43,480; Aust. Pat. 106,696; Belg. Pat. 314,428, Dec. 31, 1923; Br. Guiana Pat. 184, Apr. 10, 1924; Chil. Pat. 5484, June 25, 1925; Portug. Pat. 13,515, Dec. 11, 1924; Roum. Pat. 8913, Dec. 18, 1923; S. Afr. Pat. 1229/23, Apr. 19, 1924; Span. Pat. 87,754.

process that the anode alloy remain mobile during the refining operation, as previously explained; the aluminum-iron alloys do not meet this requirement because of their high melting points. Betts[1] suggested the reduction of clay with carbon to form an aluminum-iron-silicon alloy, followed by the electrolytic extraction of aluminum from this alloy. Such an alloy would, however, have such a high melting point as to make it impractical for use in the electrolytic refining process. The aluminum-silicon alloys are not of sufficient density to sink beneath the electrolyte in the refining cell. The aluminum-copper alloys meet both of these requirements very satisfactorily, but must be relatively low in iron and titanium. Silicon, however, in amounts from about 2 to 32 per cent of the copper content of the alloy, is a beneficial addition, and the reduction process is so carried out as to leave a substantial amount of silicon in the alloy.

An alloy low in iron and titanium can be produced by selecting raw materials of the proper purity. Where such material is not readily available, it is necessary to subject it to a preliminary purification step. For example, a clay or high-iron bauxite can be smelted, with a limited amount of carbon, in an electric furnace to produce an iron-silicon alloy containing most of the iron and titanium and a substantial portion of the silicon, together with an aluminous slag containing most of the alumina. This aluminous slag is then smelted in another furnace, with suitable proportions of copper and carbon to produce an aluminum-copper alloy of the proper composition for the electrolytic refining process. A flux, such as magnesia, can be added to reduce the melting point of the slag and facilitate the recovery of the aluminum-copper alloy.[2] If the slag itself does not contain enough silica, the necessary amount in the form of iron-free china clay or sand may be added to the charge. An alloy which has been produced in this way contained 35 per cent aluminum, 55 per cent copper, 8 per cent silicon, with less than 5 per cent iron and less than 1 per cent titanium. This alloy can be added directly to the electrolytic refining cell and aluminum of high purity produced therefrom. Frequently, however, the alloy as it comes from the electric furnace contains non-metallic impurities, such as oxides, carbides, etc., which interfere seriously

[1] BETTS, A. G., U. S. Pat. 795,886, Aug. 1, 1905.
[2] SHUMAKER, F. D., U. S. Pat. 1,611,000, Oct. 4, 1927.

with the continuous operation of the electrolytic refining cell. The major portion of these impurities may be removed by cooling the molten alloy and skimming off the dross which is formed, or a more substantial "cleaning" of the alloy may be effected by passing it through a regular Hall reduction cell. The combined effect of the solvent action of the cryolite electrolyte and the reducing action of the electrolyzing current very effectively cleans up the alloy and puts it in condition for use in the refining cell.

The impoverished copper alloy from the refining cell is returned to the process and used in the electrothermal reduction step to produce more copper alloy. From time to time it is found necessary to treat the impoverished copper alloy to remove impurities, such as iron and titanium, which accumulate in it.

APPENDIX

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